A THEORETICAL AND PRACTICAL TREATISE

ON THE

MANUFACTURE

OF

SULPHURIC ACID AND ALKALI,

WITH THE

COLLATERAL BRANCHES.

BY

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VOLUME II.

LONDON:

JOHN VAN VOORST, PATERNOSTER ROW.

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SECOND BOOK.

SULPHATE OF SODA

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CHAPTER I.

GENERAL NOTES ON SODIUM SULPHATE.

"SULPHATE" and "saltcake" are the technical names for neutral sodium sulphate (calcined Glauber's salt). Two thirds or perhaps three fourths of all the sulphuric acid made are employed for making sulphate; and a certain (but not comparatively very large) quantity of this substance is also produced in other ways. Not very much sulphate is sent into the trade as such, most of it being converted into alkali at the alkali-works; but a not inconsiderable number of manufacturers do not go beyond sulphate, with, of course, muriatic acid, bleaching-powder, &c. as by-products. These sell their sulphate to glass-makers, alkali-makers, and so forth.

Historical notes (comp. Kopp, 'Geschichte der Chemie,' iv. p. 40).—Sodium sulphate was first described by Glauber, in his treatise 'De Natura Salium' (1658). He made it from the residue remaining after the preparation of hydrochloric acid from common salt and sulphuric acid, and gave it the name *sal mirabile*, recommending it urgently for internal and external use; later on it was called after himself, *sal mirabile Glauberi*. Kunkel, however, in his 'Laboratorium Chymicum' (1716), asserts that Glauber's salt had been known as an arcanum to the Electoral house of Saxony 100 years before Glauber. On a large scale it was first produced from salt-brine at Friedrichshall in Hildburghausen, and has been known since 1767 as *sal aperitivum Fridericianum* or *Friedrichssalz*.

Properties of Sodium Sulphate.

The *anhydrous* salt is obtained in a pure state by dehydrating crystallized sulphate of soda, or by evaporating the aqueous solu-

tion at temperatures above 33° C.*; from strongly alkaline solutions anhydrous salt crystallizes out even at ordinary temperatures. In an impure state it forms the "sulphate" or saltcake of the factories. It crystallizes in the rhombic system, with an octahedral habit; its specific gravity is 2·655 (at the fusing-point, 2·104). It melts to a thin liquid at a strong red heat; Carnelly (Journ. Chem. Soc. 1878, ii. p. 280) states that the melting-point is 861°. At a white heat it volatizes; at the heat of melting iron it begins to boil and evaporates rapidly. The residue of incomplete evaporation has an alkaline reaction. On being ignited with coal it is reduced to *hepar*, according to the following equation :—

$$7\,SO_2(ONa)_2 + 13\,C = 3\,Na_2S + 2\,Na_2S_2 + 2\,CO(ONa)_2 + 11\,CO_2.$$

Carbon monoxide is *not* given off in this reaction; on the other hand, carbon monoxide does not reduce sodium sulphate at all, or only very slightly. A current of hydrochloric acid gas at a red heat converts sodium sulphate entirely into sodium chloride, sulphuric acid being set free (Boussingault); according to Hensgen (Dentsch. chem. Ges. Ber. ix. 1672), with anhydrous salt a pretty high temperature is required for this reaction; but crystallized sodium sulphate is *completely* decomposed even at ordinary temperatures. (This matter will be treated at greater length in Chapter VI.) When sodium sulphate is ignited with calcium carbonate there is *no* decomposition (Scheurer-Kestner and Kolb), which is of importance for the theory of the soda-process. A mixture of Na_2SO_4 with Al_2O_3 is not changed even at a prolonged red heat; but this takes place in the presence of water, and with especial facility in the presence of coal—sodium aluminate being formed. Fused with silica and coal, it yields silicate of soda; on fusion with iron and caustic soda, Fe_3O_4 and the sulphate of iron and sodium are formed. Its solution is decomposed very incompletely by milk of lime, into calcium sulphate and caustic soda; but according to Tessié du Motay (Deutsch. chem. Ges. Ber. v. p. 741), at a pressure of 2 to 20 atmospheres 75 to 80 per cent. of the sodium sulphate are causticized by lime.

* According to Thomsen (Deutsch. chem. Ges. Ber. xi. p. 2042) this is not anhydrous, but the monohydrated salt, SO_4Na_2, H_2O.

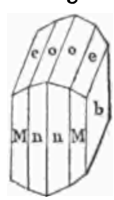
Composition of sodium sulphate.

	Anhydrous.	With $7H_2O$.	With $10H_2O$.
Na_2O	43·67	23·13	19·25
SO_3	56·33	29·85	24·84
H_2O	——	47·02	55·91

The anhydrous sodium sulphate attracts moisture even in the air, but more so in its mother liquor, in which it soon passes over into the salt with $7H_2O$. It dissolves in water at $+21°·5$ C. and higher temperatures with evolution of heat, but at $+3°$ with absorption of heat. From its solution, at temperatures above 33°, again anhydrous salt crystallizes; but below 33°, either the salt with 7 or that with $10H_2O$—the latter under most conditions, the former, for instance, from hot solutions when they cool while kept from contact with air by means of alcohol. The solutions show the phenomenon of supersaturation in the highest degree. According to Coppet (Compt. Rend. lxxviii. p. 194), two isomeric modifications of anhydrous sodium sulphate exist:—α, formed by crystallized salt efflorescing at ordinary temperatures; β, by heating above 33°. Only the α modification causes by contact the crystallization of supersaturated solutions.

The salt with $7H_2O$ (for composition and preparation see above) forms quadrilateral prisms, with two inclined end faces (fig. 1), transparent and much harder than the decahydrated salt. The crystals in the air become dull and even rough; also under their mother-liquor they become dull from the formation of the decahydrated salt.

Fig. 1.



The salt with $10H_2O$ (for composition see above) is the *crystallized Glauber's salt* proper, which separates from its solutions by evaporation in the open air or by cooling below 33°, with considerable evolution of heat. It forms very large, transparent crystals of the monoclinic system, often with many faces and, by the development of the vertical faces, assuming a long prismatic form (fig. 2). Sp. gr. 1·471. It has a cooling, afterwards bitter taste, and neutral reaction. It effloresces in the air, falling into a white powder, and loses the whole of its water, supposing the air to be pretty dry—for instance, in air of 14°·5 C. whose dew-point is at 9°·5. At 33° it melts in its water of crystallization with separation of one portion as anhydrous salt. In water it dissolves, with absorption of heat; for

Fig. 2.

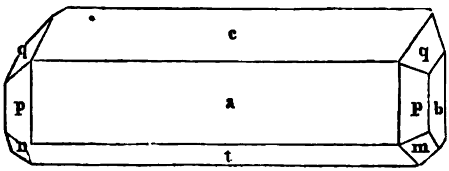
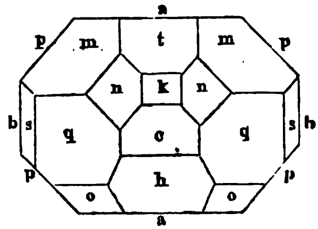


Fig. 3.



instance, on mixing 20 parts of crystals with 100 water at 12°·5 the temperature falls to 5°·7 (Rüdorff); on mixing 240 grams of crystals with an equal quantity of water at 18°, the temperature falls to 7° or 8° (Hanamann).

The solubility of the decahydrated salt in water rises from 0° to 34° C. with the temperature. At 34° and above, the solution only contains anhydrous salt, whose solubility, inversely, rises continuously on cooling from 103°·17 (the boiling-point of the saturated solution) down to 18° or 17°. Below the latter temperature the anhydrous salt cannot exist in the presence of water, but, if protected from the air, is changed into heptahydrated, with access of air or in contact with crystals into decahydrated salt. The salt with $7\,H_2O$ dissolves from 0° to 26° in increasing quantity, to the greatest extent at the latter temperature, and already at 27° is transformed into anhydrous salt. Thus sodium sulphate for temperatures from 0° to 18° presents a doubly, from 18° to 26° a triply, from 26° to 34° again a doubly different, and above 34° always the same solubility, as proved by many experiments of Loewel's (Ann. Chim. Phys. [3] 49, p. 32). Loewel states that the boiling-point of the saturated solution = 103°·17; Mulder, = 103°·5; Kremers, = 105°; Gerlach, ≐ 100°·8. The freezing-point is for each gram SO_4Na_2 in 100 cub. centims. water lowered by 0°·297 C. (Rüdorff). Supersaturated solutions solidify by themselves at −8° C., or at the ordinary temperature on contact with a crystal, with a glass rod, &c.

According to Gay-Lussac, 100 parts of water dissolve at the following temperatures :—

°	SO_4Na_2.	$SO_4Na_2+10H_2O$.
0	5·02 parts.	12·17 parts.
11·67	10·12 „	26·38 „
13·30	11·74 „	31·33 „
17·91	16·73 „	48·28 „
25·05	28·11 „	99·48 „
28·76	37·35 „	161·53 „
30·75	43·05 „	215·77 „
31·84	47·37 „	270·22 „
32·73	50·65 „	322·12 „
33·88	50·04 „	312·11 „
40·15	48·78 „	291·44 „
45·04	47·81 „	276·91 „
50·40	46·82 „	262·35 „
59·79	45·42 „	
70·61	44·35 „	
84·42	42·96 „	
103·17	42·65 „	

Solubility of the three Modifications of Sodium Sulphate according to Loewel.

Temperature.	Anhydrous salt. 100 parts water contain in the saturated state		Salt with $10H_2O$. 100 parts water contain in the saturated state		Salt with $7H_2O$. 100 parts water contain in the saturated state		
	SO_4Na_2.	Calculated as $SO_4Na_2+10H_2O$.	Calculated as SO_4Na_2.	$SO_4Na_2+10H_2O$.	Calculated as SO_4Na_2.	$SO_4Na_2+7H_2O$.	Calculated as $SO_4Na_2+10H_2O$.
°C.							
0	......	......	5·02	12·16	19·62	44·84	59·23
10	......	......	9·00	23·04	30·49	78·90	112·73
15	......	......	13·20	35·96	37·43	105·79	161·57
18	53·25	371·97	16·80	48·41	41·63	124·59	200·00
20	52·76	361·51	19·40	58 35	44·73	140·01	234·40
25	51·53	337·16	28·00	98·48	52·94	188·46	365·28
26	51·31	333·06	30·00	109·81	54·97	202·61	411·45
30	50·37	316·19	40·00	184·09			
33	49·71	305·06	50·76	323·13			
34	49·53	302·07	55·00	412·22			
40·15	48·78	290·00					
45·04	47·81	275·34					
50·40	46·82	261·36					
59·79	45·42	242·89					
70·61	44·35	229·87					
84·42	42·96	213·98					
103·17	42·65	210·67					

Specific Gravity of the Solutions of Sulphate of Soda at different Degrees of concentration at 15° C., according to Gerlach.

Per cent.	SO_4Na_2.	$SO_4Na_2+10H_2O$.
1	1·0091	1·004
2	1·0182	1·008
3	1·0274	1·013
4	1·0365	1·016
5	1·0457	1·020
6	1·0550	1·024
7	1·0644	1·028
8	1·0737	1·032
9	1·0832	1·036
10	1·0927	1·040
11	1·1025	1·044
12	....	1·047
13	....	1·052
14	....	1·056
15	....	1·060
16	....	1·064
17	....	1·069
18	....	1·073
19	....	1·077
20	....	1·082
21	....	1·086
22	....	1·090
23	....	1·094
24	....	1·098
25	....	1·103
26	....	1·107
27	....	1·111
28	....	1·116
29	....	1·120
30	....	1·125

At 19°, according to Schiff (Ann. Chem. Pharm. cx. p. 70).

Spec. grav.	Per cent. $Na_2SO_4+10H_2O$.	Per cent. Na_2SO_4.
1·0040	1	0·441
1·0079	2	0·882
1·0118	3	1·323
1·0158	4	1·764
1·0198	5	2·205
1·0238	6	2·640
1·0278	7	3·087
1·0318	8	3·528
1·0358	9	3·969
1·0398	10	4·410
1·0439	11	4·851
1·0479	12	5·292
1·0520	13	5·733
1·0560	14	6·174
1·0601	15	6·615
1·0642	16	7·056
1·0683	17	7·497
1·0725	18	7·938
1·0766	19	8·379
1·0807	20	8·820
1·0849	21	9·261
1·0890	22	9·702
1·0931	23	10·143
1·0973	24	10·584
1·1015	25	11·025
1·1057	26	11·466
1·1100	27	11·907
1·1142	28	12·348
1·1184	29	12·789
1·1226	30	13·230

Sodium sulphate is almost insoluble in absolute alcohol at ordinary temperatures, a little more so in alcohol acidulated with sulphuric acid. Therefore alcohol precipitates sodium sulphate from a saturated cold solution. In dilute alcohol it is more soluble; the saturated solution, according to Schiff (Ann. Chem. Pharm. cxviii. p. 365) contains at 15° C.:—

Alcohol of spec. grav.	Per cent. C_2H_6O by weight.	Per cent. of $SO_4Na_2+10H_2O$.
1·000 (water)	0	25·6
0·976	10	14·35
0·972	20	5·6
0·939	40	1·3

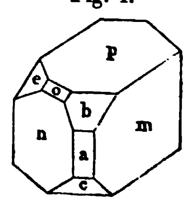
It is soluble in glycerine, less so in strong acetic acid, soluble in hydrochloric acid with strong evolution of heat, but with decomposition (see above). In some saline solutions it is more easily soluble than in pure water—for instance, in solutions of potassium sulphate, magnesium sulphate, potassium chloride, potassium nitrate, in which cases of course all the bases in the solution must be regarded as combined or combinable with all the acids. On pounding together sal-ammoniac and Glauber's salt, the dry mixture becomes damp, the temperature being lowered at the same time, and a mixture of ammonium sulphate, sodium chloride, and water being formed, of which the latter previously existed in the crystals.

The other sodium sulphates, except the neutral one, have no technical importance by themselves, and only serve as transition stages in the manufacture of the neutral sulphate; we will now describe them very briefly.

1. *Three-quarters-saturated sulphate,* $Na_3H(SO_4)_2$, observed by Thomson and Mitscherlich, crystallizes first on recrystallizing the semisaturated sulphate. Brilliant, often needle-shaped crystals of the monoclinic system, with many faces, stable in the air.

2. *Hydrosodic sulphate* (*acid sodium sulphate, sodium bisulphate*). $SO_4NaH = SO_2\langle{}^{ONa}_{OH}$. Formed by heating common salt with two equivalents (=one molecule) of sulphuric acid, or of neutral sulphate with more sulphuric acid; on dissolving it in hot water and evaporating it above 50° C., anhydrous crystals, and by cooling hydrated crystals are separated.

Fig. 4.



a. The *anhydrous crystals* are transparent, long, quadrilateral prisms with oblique end faces (fig. 4), very brilliant also on drying; in the air they quickly become dull, without deliquescing. Sp. gr. 1·8. They melt at 149° (Thomson), or above 315° C. (Graham), without any decomposition, and only at a higher

temperature give out sulphuric acid. According to Kraut one portion splits up into sulphuric hydrate and neutral salt, another into water and pyrosulphate: $2SO_4NaH = Na_2S_2O_7 + H_2O$. Water decomposes the salt into neutral sulphate and free sulphuric acid; in moist air, lying on blotting-paper, the crystals (as also those of *b*) leave effloresced neutral salt behind. Alcohol deprives the powdered salt of all free acid.

b. Hydrated salt, SO_4NaH, H_2O, often forms very large, transparent crystals of the monoclinic system (figs. 5 & 6) which mostly have a prismatic appearance. They attract water in moist air.

Fig. 5.

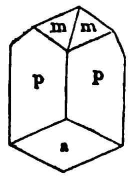
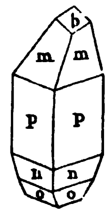


Fig. 6.



3. *Quarter-saturated sulphate*, SO_4NaH, SO_4H_2, crystallizes on cooling a solution of $1\ SO_4Na_2$ in not quite $7\ SO_4H_2$. It fuses at about 100°. Long, colourless, brilliant prisms.

4. *Sodium pyrosulphate*, $S_2O_7Na_2 = \begin{matrix} SO_2-ONa \\ \rangle O \\ SO_2-ONa \end{matrix}$, remains behind on heating sodium chloride with sulphuric anhydride

$$(2\,NaCl + 4\,SO_3 = Na_2S_2O_7 + S_2O_5Cl_2,$$

Rosenstiehl) and on igniting the acid sulphate (compare No. 2); it is also separated along with the latter from a solution of sulphate in fuming oil of vitriol; it can also be precipitated from the fuming oil of vitriol of trade (in which it always occurs) by boiling nitric acid, aqua regia, chlorine, ether, or alcohol. It probably also occurs in ordinary furnaced saltcake. Exposed to a bright red heat it splits up into neutral sulphate and sulphuric anhydride, according to the equation $S_2O_7Na_2 = SO_4Na_2 + SO_3$; this is the cause, at least partly, of the thick white vapours which calcined saltcake emits on being drawn out of the furnace.

The *sulphate or saltcake of trade* is a more or less finely granulate mass, often containing larger lumps of melted substance; the latter are always to be suspected of containing a high percentage of sodium chloride, and often entirely consist of this internally. The finer grain a sulphate possesses, the better it is on the whole. Its colour when hot, as it is drawn out of the furnace, is a bright lemon-yellow—if very rich in free acid, even brownish—if much iron is present, brownish red. In the cold it is yellowish or greenish

white, often pure white. A dirty grey colour and a granular fritted consistence show that the decomposition of the common salt is incomplete.

The analyses given on p. 13 show the composition of commercial sulphate.

The following analyses by Theilkuhl (from Knapp, ii. p. 396) show the "free acid" as acid sulphate:—

	From Nienburg.	?	From Lüneburg.	From Oker.
SO_4Na_2	96·2	93·3	90·5	65·9
SO_4NaH	0·5	2·4	8·0	31·8
NaCl	1·5	2·9	0·03	—
$Fe_2(SO_4)_3$	0·5	0·5	0·3	1·6
Sand	0·5	0·3	0·1	0·2
Moisture	0·8	0·8	1·1	0·4

(That from Oker is evidently nitre-cake.)

Analysis of Sulphate.

Pure sulphate is quite white, forms a clear solution in water, has a neutral reaction, shows no trace of chlorine when treated with silver nitrate, does not throw down any precipitates under the action of sulphuretted hydrogen, ammonium sulphide, sodium or ammonium carbonate, or potassium ferrocyanide. The sulphate of trade is tested in the following way:—Mostly only the foreign constituents are estimated, and the pure SO_4Na_2 calculated from the difference. If one only wants to test the *sulphate for one's own use* (for alkali-making), where it is only a check on the manufacture, the following simple process is sufficient: 10 grms. of sulphate are weighed, dissolved in 200 cub. centims. warm water, 20 cub. centims. (=1 grm.) taken out with a pipette, and, after litmus has been added, neutralized with standard caustic; by this the free acid is found. A second sample of 20 cub. centims. is neutralized by the same quantity of caustic as was required in the first test; and a few drops of potassium chromate are added, and the NaCl titrated by silver solution. If, on the other hand, an analysis is to be made *for sale*, a somewhat more accurate process must be employed. 10 grms. are calcined in a porcelain dish with the addition of a little ammonium carbonate, and weighed again, by which operation the moisture and the free acid are found. The latter is estimated by itself in a fresh uncalcined sample in the same way as described above. The calcined sulphate is dissolved in water and filtered, the

	I. Chandelon. English. Made in iron.	I. Chandelon. Belgian. Made in iron.	I. Chandelon. Belgian. Made in lead.	II. Brown. English.	III. Theilkuhl and Linden.	IV. Muspratt (Liverpool).	V. De Koninck.	VI. Tate. English.	VII. Simmonds. English.	VIII. Plunkett. Hargreaves's sulphate.	IX. Davis. From a blind roaster.	X. Davis. From an open roaster.	XI. Davis. Made by Hargreaves's process.
	p. c.	p. c.	p. c.	p. c.	p. c.	p. c.	p. c.	p. c.	p. c.	p. c.	p. c.	p. c.	p. c.
Na_2SO_4	·93·15	94·10	95·29	96·22	93·1	96·515	93·36	95·25	96·50	99·24	94·393	96·137	97·824
$CaSO_4$	1·21	0·84	0·86	0·97	—	0·923	1·16	1·25	1·00	—	1·139	1·148	1·046
$MgSO_4$	—	0·35	0·77	0·29	—	—	—	—	—	—	—	—	—
$Al_2(SO_4)_3$ ...	0·15	0·16	0·41	—	—	—	—	—	—	—	—	—	—
$FeSO_4$	0·75	0·97	0·14	0·23	0·4 (Fe_2O_3)	0·191 (Fe_2O_3)	0·42 (Fe_2O_3 $+Al_2O_3$)	0·50 (Fe_2O_3 $+SiO_2$)	0·30 (Fe_2O_3)	—	0·682	0·558	0·522
$PbSO_4$	—	—	0·05	—	—	—	—	—	—	—	—	—	—
NaCl	1·66	0·14	0·37	1·09	0·6	1·345	2·04	1·75	0·75	0·08	2·632	0·234	0·744
SO_3	1·44	2·52	1·30	0·88	—	0·616	1·36	1·00	1·00 (+HCl)	0·20	0·955	1·820	0·022
H_2O	1·28	0·48	0·29	—	4·5	0·187	1·45	0·25	0·20		0·087	—	—
Insoluble ... (sand).	0·26	0·42	0·51	0·31	0·3	0·130	0·21	—	0·25	0·48 (+Fe_2O_3)	0·112	0·073	0·042

I. From 'Moniteur Scientifique,' 1864, p. 51.
II. & III. From Knapp's 'Chem. Technologie,' ii. p. 395.
IV. From Muspratt's 'Chemistry,' ii. p. 913.
V. From Kerl-Stohmann's 'Chemistry,' v. p. 300.
VI. From 'Chemical News,' xxix. p. 144.
VII. From 'Chemical News,' xxix. p. 184.
VIII. From 'Dingler's Journal,' ccxviii. p. 425.
IX.–XI. From 'Chemical News,' xxxii. p. 174.

residue weighed, treated with hydrochloric acid, and the iron in the solution estimated; the separation of alumina, which only occurs in very small quantity, is hardly ever made. The insoluble portion is calculated as sand. In the filtrate the chlorine can be estimated as above, and the lime by precipitating by ammonium oxalate. It is, however, preferable to omit the calcining, and to proceed in this manner:—The sample is dried at 100° C., in which case no acid escapes, weighed, dissolved in water, the weight of the residue (sand and a little ferric oxide) estimated; and in the solution, which is reduced to a definite volume, free acid, chlorine, lime (to be calculated as sulphate), iron, &c. are estimated separately. In this case there is no danger of expelling any HCl. At some English works 0·75 per cent. is always reckoned for silica and ferric oxide, the free acid and undecomposed NaCl estimated, and the remainder taken as Na_2SO_4. This calculation neglects the lime, which is not allowable; for even with common pan-salt there is often upwards of 1 per cent of SO_4Ca, and with rock-salt even more than that.

We observe here that the term "free acid" is used for all that is indicated by neutralizing with standard caustic—such as half of the acid of the bisulphate or pyrosulphate and all the acid combined with alumina and ferric oxide. It is mostly computed as SO_3. The iron occurs partly as ferrous sulphate, partly as ferric sulphate, partly as ferric oxide (insoluble in water).

De Koninck ('Revue Universelle,' xxxv. p. 366, xxxix. p. 394; 'Chemical News,' xxxiii. p. 252) employs the following plan. He dissolves 50 grms. sulphate and filters into a litre flask; the residue is washed and ignited. The filtrate is reduced to 1 litre; 300 cub. centims. of this are used for estimating the free acid by titrating with ammonia, the latter being added till ferric hydrate begins to precipitate; a little litmus is added and again standard sulphuric acid, till the liquid just turns reddish. Al_2O_3 and Fe_2O_3 are estimated by adding chlorine- or bromine-water to 200 cub. centims. of the solution, precipitating by NH_3, filtering, &c. In the filtrate the lime is estimated by ammonium oxalate, the precipitate is washed, ignited, converted into calcium sulphate by sulphuric acid, and weighed as such. Or all three may be estimated together, without filtering off Al_2O_3 and Fe_2O_3, in which case, after adding sulphuric acid and igniting again, Al_2O_3, Fe_2O_3, and $CaSO_4$ remain. Sodium chloride is estimated in 100 cub. centims, as usual, by standard silver nitrate with potassium chromate as indicator, the

free acid having been neutralized by a solution of borax. De Koninck considers the estimation of moisture by heating to 100° C. inexact, because, on the one hand, at that temperature some water still remains, and, on the other hand, the bisulphate already acts on the sodium chloride, and hydrochloric acid is given off. He therefore estimates the water indirectly by heating 2 grms. of sulphate in a covered platinum crucible up to fusion, at which point water, sulphuric acid, and hydrochloric acid escape [an addition of ammonium carbonate would be useful in this case], and deducts from the loss, first, the "free" sulphuric acid; secondly, for each 117 parts of common salt decomposed (estimated by dissolving and titrating the NaCl still present), he adds another 25 parts ($SO_4H_2=98$, $2\,HCl=73$)—that is, to 1 NaCl 0·214.

Natural Occurrence of Sodium Sulphate.

Sodium sulphate is found in nature both in the anhydrous state, as *thenardite* and as crystallized salt (*mirabilite*, $SO_4Na_2+10\,H_2O$) —also in combination with calcium sulphate (as *glauberite*), as a constituent of natural soda, dissolved in mineral waters, sea-water, &c. In some places Glauber's salt is obtained from these sources on an industrial scale.

Thenardite (SO_4Na_2) crystallizes rhombically, in pretty large pointed pyramids combined into crusts; its surface is rough, its taste faintly saline. In the air it becomes dull by absorbing water. Its principal occurrence is in the rock-salt beds at Espartinas, near Aranjuez, also in Peru (Tarapaca &c.).

In combination with water, sodium sulphate occurs in several species of minerals; with 10 molecules of water as *mirabilite*, mostly only as efflorescences and crusts on rocks or old walls, but in larger quantities at Mühlingen, in the Aargau, in gypsum, in the salt beds at Hallstadt and Aussee. Other species, containing magnesia, are *reussin*, *loeweite*, and *bloedite* (from Ischl).

In the Ebro valley, especially near Lodosa, a few years ago large beds of hydrated sodium sulphate were found, as glassy layers from about 2 feet up to several yards in thickness, between beds of clay and gypsum. Similar beds have been found at Calatayud and Corvora, near Santander, in Catalonia, Old Castile, and other places. These beds are principally worked at Lodosa, Alcanadra, and Androsilla, and also at Calmenar de Oreja, in the province of Madrid. This Spanish sulphate is quite free from iron, and is consequently

very well adapted for glass-making; but most of the English consumers have given up its use again, owing to its variable quality.

Other occurrences of more or less hydrated sulphate are:—in Hungary, Switzerland, Italy, France (St. Rambert), as *exanthalose* with 20 per cent. water (a volcanic product of Vesuvius), in a cavern at Kailua, on the island of Hawaii; as an efflorescence on the Siberian and Caucasian steppes, on the limestone below the falls of the Genesee, and on the Sweetwater River in the Rocky Mountains.

Analyses of different Minerals of this kind.

	Mirabilite of St. Rambert.
	p. c.
Na_2O	20·0
MgO	0·7
SO_3	26·0
HCl	trace.
H_2O	53·0

	Thenardite. Spain.	Thenardite. Tarapaca.
	p. c.	p. c.
Na_2SO_4	99·78	97·48
Na_2CO_3	0·22	—
Insoluble	—	2·19

	Bloedit (John).	Reussin (Reuss).	Astrakanite from the mouth of the Volga (Göbel).
	p. c.	p. c.	p. c.
Na_2SO_4	33·34	66·04	41·00
$MgSO_4$	36·66	31·35	35·18
$CaSO_4$	—	0·42 (incl. sand)	1·75
$MnSO_4$	0·33	—	—
$FeSO_4$	0·34	—	—
$NaCl$	0·33	—	—
$CaCl_2$	—	2·19	—
$MgCl_2$	—	—	0·33
H_2O	22·00	—	21·56

Very copiously found is the double sulphate of sodium and calcium, called *glauberite*,—for instance, in the salt-mines of Villarubia in Spain, of Vic in France, of Berchtesgaden in Bavaria, of Stassfurt, in the province of Tarapaca, &c. Analyses of it have shown:—

	Varangéville (Pisani).	Villarubia (Brogniart).	Berchtesgaden (Kobell).
	p. c.	p. c.	p. c.
Na_2SO_4	50·50	51	48·6
$CaSO_4$	48·78	49	51·0
Clay	0·40	—	—

	Atacama (Hayes).
	p. c.
Na_2O	21·32
CaO	20·68
Fe_2O_3	0·14
SO_3	57·22

Very frequently sodium sulphate is found along with natural soda (trona) and common salts—for instance, in the water of the lakes of the Araxes plain and the salts crystallizing out of it, which have been studied especially by Abich (Journ. f. prakt. Chem. xxxviii. p. 4). Both on the surface and at the bottom of the lakes such salts are separated, strange to say, almost free from water.

The following analyses show the composition of these salts, as well as of the pink mother-liquor, containing 30·63 per cent. of salt, and of that of some alkaline small pools in the neighbourhood, containing 34·7 per cent. of salt.

	Salts at the surface.	Salts at the bottom.	Mother-liquor salts.	Alkaline pools (dry).
	p. c.	p. c.	p. c.	p. c.
Na_2SO_4	80·56	78·44	18·18	15·55
Na_2CO_3	16·09	18·42	12·08	68·9
$NaCl$	1·62	1·92	69·73	15·5
H_2O	0·55	1·18	—	—

CHAPTER II.

ENUMERATION OF THE PROCESSES FOR OBTAINING SULPHATE.

Only a very small portion of the sodium sulphate is prepared in the crystallized state as Glauber's salt, principally that serving for pharmaceutical purposes, but now mostly used only in veterinary practice; all the rest is made as calcined sulphate or "saltcake," the smaller portion of it being used as such (for instance, in glass-making), the larger portion being at once converted into alkali.

The different processes for preparing sulphate may be divided into those in which it is the principal product, and those in which it is a by-product. As the principal product, nearly all the sulphate is obtained by decomposing common salt with sulphuric acid, or common salt with sulphurous acid in the presence of air (according to Longmaid, Hargreaves, &c.). We shall treat of these processes later on; at present we will turn our attention to

Sulphate of Soda obtained as a by-product.

In most natural waters small quantities of sodium sulphate occur, or, to speak more correctly, of sulphates and sodium salts at the same time. Preparation of Glauber's salt from this source on an industrial scale is only exceptionally possible, chiefly when the liquid has been previously concentrated for other purposes, and Glauber's salt can be got from the mother-liquors. This is especially the case in the manufacture of common salt from sea-water or from brine; Glauber's salt can be made both from the mother-liquors and the pan-scale obtained in this manufacture.

The preparation of Glauber's salt by means of kieserite might also be enumerated here, since that mineral itself is only a by-product.

Lastly, we must mention the manufacture of sodium sulphate, usually in a very impure state, as a by-product of sundry chemical manufactures—above all,

1st, *in manufacturing muriatic acid* from common salt and sulphuric acid, in cast-iron cylinders (see below) and in glass retorts. Here muriatic acid is the principal product; and in manufacturing it less than the theoretical quantity of sulphuric acid is employed, both because common salt is much cheaper than sulphuric acid and may rather be in excess, and because contamination of the distilling hydrochloric acid by sulphuric acid is thus avoided. This manufacture, formerly carried on in several places on the Continent and in the suburbs of London, has now almost entirely ceased. The product used to be called *cylinder-cake* or *saltcake,* the latter in the north-east of England, whilst this expression in the west always meant ordinary calcined sulphate; it contained from 7 to 10 per cent. of NaCl in excess; and its use was restricted chiefly to glass- and alkali-works, where it was mixed with a little more sulphuric acid in the ordinary sulphate-furnaces and made into finished sulphate. We shall touch upon this more in detail in the third Chapter.

2nd. *In the manufacture of nitric acid* a product is obtained which, contrary to the former one, contains much free sulphuric acid, because in this case, of the two raw materials, sodium nitrate is the more valuable, sulphuric acid the less valuable, and because only by an excess of sulphuric acid can the nitric acid be properly expelled. Especially where nitric acid is made at vitriol-works, a large excess of the latter acid is generally used; and such sulphate, known as "nitre-cake," "salonix" (=sal enixum), or "sally," occurs with 30 per cent. and upwards of free acid, calculated as SO_3. Those nitric-acid manufacturers who have to buy their sulphuric acid are more economical in this respect, and often send the residue from the retorts into the trade with only 7 to 10 per cent. of "free" SO_3. Of course free SO_3, or even SO_4H_2, is never present, but merely acid sulphate, SO_4NaH. The quantity of acid sulphate made in this way is very considerable. Apart from its use in making vitriol, enormous quantities of nitric acid are required in the manufacture of coal-tar dyes (for instance, nitrobenzene), picric acid, arsenic acid, phthalic acid, and in innumerable other cases,—furthermore, for making gun-cotton, nitroglycerine, &c.

A small portion of this acid sulphate, if some statements may be believed, is worked up for fuming oil of vitriol in France (comp.

Vol. I. p. 638); at any rate the largest portion finds its way into alkali-works, where it is made into neutral sulphate by calcining with common salt. Usually a certain quantity of it is put into the decomposing-pans along with the ordinary charge, leaving out a corresponding quantity of sulphuric acid.

Dunlop's patent process of 1853, which is still carried out at St. Rollox, by which the nitre-gas required for the vitriol-chambers is derived from heating sulphuric acid with common salt and nitrate of soda (comp. Vol. I. p. 320), also furnishes acid sodium sulphate as a by-product.

3rd. Smaller quantities of sulphate are obtained, for instance:—in the manufacture of *sal-ammoniac* by subliming ammonium sulphate with common salt; in that of *corrosive sublimate* from mercuric sulphate and common salt; in *amalgamating silver-ores*; in *roasting copper-ores* with common salt; in making *aluminium chloride* from common salt and alum; in *purifying mineral oils* by mixing the sulphuric acid and caustic lye used in purifying, and scumming off the tar (exactly described by Breitenlohner in 'Dingler's Journal,' clxxv. p. 459); in neutralizing *organic sulpho-acids* containing a large excess of sulphuric acid by soda; and especially from the alkaline fusions in the manufacture of resorcine, alizarine, &c. Kessler (Wagner's Jahresb. 1859, p. 244) proposes to get sodium sulphate from the zinc sulphate of galvanic cells by means of common salt. P. W. Hofmann, in an analogous way, recovers the same by washing the cinders from burning pyrites containing zinc (comp. Vol. I. p. 580).

In most of the cases just mentioned the sulphate, owing to its low price, cannot be recovered economically, unless at least the crystallized salt is obtained without any expense of evaporation, by spontaneous crystallization. Usually the solutions containing the sulphate are run to waste, because they cannot be profitably worked up.

Manufacture of Sulphate from Mother-liquors and By-products of Salt-works and Salt-gardens.

(1) *From mother-liquors.*—In these there are always chlorides and sulphates of sodium, magnesium, &c. present (calcium chloride has already at a previous stage been converted into gypsum, which has got into the pan-scale); and, according to the temperature, the acids and bases combine in different ways. In the salt-gardens (*marais salants*) on the Mediterranean, worked according to the

process of Balard and Merle (much the same as a process introduced into the Schoenebeck salt-works by Hermann at the beginning of the present century), concentration by spontaneous evaporation, after the purer common salt has been separated, is allowed to go on till (at 58° to 64° Tw.) a crystalline deposit of equal parts of Epsom salt and common salt (*sels mixtes*) has been formed. This is drained, in order to remove, as much as possible, the deliquescent magnesium chloride, dissolved in water up to the point of saturation (55° to 57° Tw.), and the solution cooled in winter by natural cold, in summer by Carré's freezing-machines. In this case the constituents group themselves in such a way that Glauber's salt crystallizes out, and magnesium chloride remains in the mother-liquor, thus :—

$$MgSO_4 + 2NaCl = Na_2SO_4 + MgCl_2.$$

The decomposition is most complete if to one molecule of Epsom salt there are three instead of two molecules of common salt; then, on cooling to $-1°$ or $-2°$ C., almost four fifths of all the sulphate which the mixed salts can furnish are actually obtained. It is drained in the cold; and from the mother-liquors at $+5°$ to $+6°$ C. (in autumn) crops of Epsom salt are obtained, which, dissolved with common salt and cooled, furnish new quantities of Glauber's salt. Too much cooling must be avoided, as otherwise carnallite ($MgCl_2 + 2KCl + 6H_2O$) crystallizes out, which ought to happen only with the last mother-liquors. The crude Glauber's salt is sometimes purified by dissolving in tepid water and crystallizing.

The sulphate prepared in this way could not possibly compete with that of the alkali-works, unless the common salt and the potassium chloride, being the principal products, paid the expense of the process.

(2) *From the pan-scale of salt-works*, which essentially consists of the sulphates of sodium and calcium. It is lixiviated with water; gypsum, being insoluble in a solution of sodium sulphate, remains behind. On the large scale, four tanks are ranged side by side, and charged with pan-scale and tepid water. After 24 hours the liquid is run off by a plug-hole in the bottom, pumped into the second tank, kept there for another 24 hours, and then conveyed into the third, and ultimately into the fourth tank. The first tank has in the meantime been filled with fresh water, which is repeated four times; it is then emptied and the residue of gypsum sold as manure. The liquid from the fourth tank is again

brought into contact with fresh pan-scale in the first tank, and thus completely saturated. Liquors of 42°–44° Tw. are thus obtained in summer, which are either kept till winter in wooden tanks, whereupon Glauber's salt crystallizes out in frosty weather, or they are concentrated by evaporation, filtered through canvas bags, and allowed to crystallize at ordinary temperatures. Long, shallow wooden troughs lined with lead, say 20 feet long by 6 feet wide, serve as coolers; the liquid should not stand in them deeper than 3 inches, because otherwise too large crystals are formed, which are not liked in the trade. As soon as the crystallization sets in, a wooden rake is drawn from one end of the cooler to the other; this gentle movement causes the separation of many individual crystals, which afterwards grow especially in the longitudinal direction, and thus acquire the peculiar acicular appearance exhibited by the so-called English Glauber's salt. If the liquid were moved too much, or stirred about, as in making Epsom salt, instead of well-formed crystals only a muddy crop would be obtained. If, on the other hand, the liquid is allowed to remain in perfect rest, the salt crystallizes principally at the sides and the bottom in the shape of large, firm, well-formed crystals, which must be detached with a chisel and broken up.

When the cooling is complete, the mother-liquor is drawn off by a siphon, the salt is put into a tub with a plug-hole in the bottom, and the liquor drained off clear. The remaining mother-liquor is removed by sprinkling cold water on the salt with a watering-can, allowing it to stand for 24 hours and drain. The salt is dried on wickerwork trays, in summer in an open place protected from dust, in winter in a gently heated stove. The crystals are not left in contact with air any longer than until they show the first traces of effervescence on their surface; otherwise they would become unsightly in appearance (Kerl-Stohmann's Chemie, v. p. 253).

On working-up kelp, sodium sulphate is also obtained, after the crops of potassium sulphate, potassium chloride, common salt, and sodium carbonate have been got out, just before the working for iodine commences.

Manufacture of Sodium Sulphate from Stassfurt Kieserite.—Kieserite ($MgSO_4 + H_2O$) is obtained at Stassfurt from the residue remaining in the treatment of the "Abraumsalz" for potash salts. This residue contains 55 to 60 per cent. of common salt, 25 to 30

per cent. of magnesium sulphate, a little potassium chloride, anhydrite, clay, boracite, and water. The working-up of kieserite, first for Epsom salt ($MgSO_4 + 7\ H_2O$) and then for other chemicals by means of the same, was first proposed by Clemm (French patent of Oct. 6th, 1863; Wagner's 'Jahresbericht,' 1864, p. 256). Whilst his other proposals have not turned out successful, his process for separating the kieserite itself is employed up to the present time. The residue from dissolving the Abraumsalz is treated with a current of cold water in a tub with a perforated false bottom; thus the kieserite is washed away in the state of flour, the rock-salt being partially dissolved and partially remaining behind in larger pieces. The water, with the particles suspended therein, is separated from the coarser particles by a fine sieve, and then subjected to fractional settling; thus the kieserite is obtained in a comparatively pure state, viz. with 55 to 60 per cent. $MgSO_4$, 8 to 10 per cent. $CaSO_4$, 2 to 4 NaCl, the remainder being H_2O. By exposure to the air and treatment with hot water, Epsom salt can easily be obtained from it, and from this also Glauber's salt by Balard's process; but for this purpose, since 1865, the crude residue from the dissolution is usually employed, which at the same time contains the necessary common salt. At first great difficulties were met with in making and working up large quantities of liquor in the cold of winter. The employment of ice-making machines seemed too expensive; and even the idea of making from the residues, directly after dissolving the potassium salts, a liquor adapted for obtaining sodium sulphate, and keeping this in water-tight brick tanks till winter, was found difficult to realize, as the tanks could not be kept tight. After sufficient experience had in this way been gained, manufacturers have reverted to making the solutions of Glauber's salt only in winter and during sufficiently frosty weather; the residues obtained during other seasons from dissolving the potash salts, first weathered in heaps, along with those made in winter, are quickly dissolved by steam in vessels provided with agitating machinery, settled, and exposed to the frost in large wooden coolers. At one works the residues are simply dissolved by tepid water run over them in tubs provided with a perforated false bottom. This process can only be employed for completely weathered residues, and does not yield as much as the former. Such residues, weathered for some years, contain all the kieserite already converted into Epsom salts. An analysis showed:—

$MgSO_4$	14·49
Na_2SO_4	13·96
$CaSO_4$	2·26
NaCl	27·09
KCl	1·60
Insoluble	10·48
Water	30·12

The fresh residues must be freed from adhering magnesium chloride and carnallite by washing with water, because these greatly interfere with the crystallization of Glauber's salt, which, however, is much assisted by an excess of common salt (see above); the residues are therefore picked in such a way that they contain at once 4 molecules of NaCl to 1 of $MgSO_4$.

The crude Glauber's salt obtained in this way has the following average composition:—

Na_2SO_4	40·22
NaCl	1·23
$MgSO_4$	0·47
$MgCl_2$	0·92
$CaSO_4$	1·12
Insoluble	1·40
Water	54·64

It is useless for most purposes, on account of its impurities, and is therefore either dissolved and recrystallized (*refined Glauber's salt*) or converted into calcined sulphate. In both forms the glass-works prefer it to the sulphate made by decomposing common salt with sulphuric acid, as it is almost completely free from iron and quite as free from acid. The average composition of the calcined sulphate is:—

	1st quality.	2nd quality.
Na_2SO_4	97	94
$CaSO_4$	1·1	1·1
NaCl	1·6	2·5
Insoluble	0·3	2·2
Fe_2O_3	0·04	0·07

The crystallized Glauber's salt can be obtained either in large

crystals similar to soda, or in small ones similar to Epsom salt; both are unfortunately much used for adulterating this salt—especially soda, as Epsom salt does not differ much in price from Glauber's salt.

Following this process, the works of the Leopoldshall United Company in the winter 1872–73 made about 3750 tons, in 1873–74 about 7500 tons, in 1874–75 12,500 tons of crude Glauber's salt.

The coolers have a surface of 12,000 square metres, and in frosty nights furnish up to 150 tons of crude crystals in 24 hours. If all the Leopoldshall and Strassfurt works would work up their residue in a similar manner, 35,000 tons of crystals, or 11,500 to 12,000 tons of calcined sulphate could be obtained; but as this takes much space and capital, and the cost price of the sulphate is hardly less than that made in the usual way, many factories prefer only washing for crude kieserite. (This description is by Dr. Frank, in Hofmann's 'Bericht,' 1875, p. 363.)

Clemm's proposal of 1863, mentioned above, was the following. To 1 molecule of NaCl 2 equivalents (= 1 molecule) of kieserite were to be employed, because in the case of equal equivalents only half of the NaCl is decomposed and a double salt, Na_2SO_4 and $MgSO_4$, is formed. If the double equivalent of kieserite is taken and the mixture boiled sufficiently long with water, all the NaCl can be decomposed. The solution is evaporated to dryness and the residue treated with steam at a red heat: HCl escapes; and the double salt remains behind, mixed with magnesia. These are separated by lixiviation; and on evaporating the solution the sodium sulphate is separated in an anhydrous state. These reactions, however, are not quite so smooth; and the sulphate thus obtained is too dear (Michels, in Wagner's 'Jahresbericht,' 1865, p. 288).

Manufacture of Sulphate from Common Salt.

The following processes have been proposed for making sulphate from common salt as a principal product:—

1. *Heating common salt with sulphuric acid.*—This is the process generally employed, and will afterwards be described in detail.

2. *Heating common salt with sulphurous acid and atmospheric*

air.—This is the process of Hargreaves and Robinson, also to be described in detail hereafter.

3. *Heating common salt with metallic sulphides, especially iron- and copper-pyrites.*—The idea of making sodium sulphate by roasting common salt with pyrites is at all events a very old one; Berzelius ('Lehrbuch der Chemie,' 1836, vol. iv. p. 153) mentions it as a proposal, with the addition of powdered coal. The fact that pyrites, or brown coal containing the same, under these circumstances, yields sodium sulphate on lixiviation, must have been already known in the last century; for the French Commission of 1792, in their official Report, recommended this mode of preparation as preferable to that proposed by Leblanc (Wagner, 'Jahresbericht,' 1857, p. 103). This judgment certainly was proved to be incorrect in practice; and the process was probably never carried out to any extent on a large scale. But attention was soon drawn to the fact that in the roasting of metallic sulphides with common salt, occurring in metallurgical processes, a large portion of the sulphur is found in the calcined mass as sodium sulphate; and Glauber's salt derived from this source was actually sent into the market. This may have been the occasion of Longmaid's bringing out a renewal of this process, which was carried on energetically for a number of years and attracted great attention, but in the end had to be given up. His first patent dates from October 20th, 1842; a second one of January 1st, 1844, makes no essential addition. He proposed to treat metallic sulphides with common salt, in the proportion of at least 60 NaCl to 40 sulphur, in a reverberatory furnace with four beds, each of which is a little higher than that nearer the fire; the mixture is charged upon the highest bed and gradually brought down. The product on lixiviation furnishes sodium sulphate, common salt, and copper salts. The copper is precipitated by metallic iron, the iron salts precipitated by lime, and the sodium sulphate obtained from the mother-liquor by evaporation. The access of air during the roasting must be exactly regulated for each part of the furnace, so that at first only ferric sulphate is formed, from which, at a higher temperature, sulphuric anhydride is liberated; this with common salt yields sodium sulphate, free chlorine, and sulphurous acid, but very little of the latter in the presence of air. The following reactions may take place in the presence of air:—

$$2\,FeS_2 + 8\,NaCl + 16\,O = 4\,Na_2SO_4 + Fe_2Cl_6 + 2\,Cl,$$
$$2\,FeS_2 + 8\,NaCl + 19\,O = 4\,Na_2SO_4 + Fe_2O_3 + 8\,Cl\,;$$

or, in the presence of steam,

$$2\,FeS_2 + 8\,NaCl + 4\,H_2O + 15\,O = 4\,Na_2SO_4 + Fe_2O_3 + 8\,HCl.$$

The latter reaction is only a secondary one in the original process of Longmaid. It is, however, much more complete than the former; and therefore in Hargreaves's process steam is always employed. The addition of small coal frequently made (not by Longmaid) only serves as fuel, and is not only unnecessary, since no great heat is required, but even injurious, by reducing sulphate to sulphide.

By being only gradually moved from the coolest to the hottest part of the reverberatory furnace, the common salt is only gradually transformed into sulphate, and the mixture becomes more capable of withstanding a high temperature without melting. This easy fusibility of the mass is just one of the principal difficulties of the process, because it necessitates the heat being moderate, rendering the decomposition very slow, and very incomplete if any fused portions are present. It is also impossible to avoid a loss of sulphur in the shape of sulphurous acid in this operation. The advantage of the process at the time of its introduction lay in the possibility of working up worthless small ore and of obtaining from the residue small quantities of copper and tin, not otherwise recoverable. The sulphate certainly contained too much common salt to be employed directly in alkali-works, and had first to be heated with sulphuric acid in ordinary decomposing-pans. Longmaid conveyed the gas generated in calcining through wooden flues submerged in water, where muriatic acid and ferric chloride condensed, whilst chlorine remained behind and was used for making bleaching-powder; of course this was only very weak, and had to be brought up to the usual standard by chlorine obtained in the usual way, which no doubt was found impossible in practice.

Longmaid's process was carried out for a number of years by the inventor himself at St. Helen's in Lancashire, at Ardrossan, and at Wallsend-on-Tyne. In Scotland (Wagner's Jahresb. 1861, p. 171) a slate containing pyrites (say 10 to 30 per cent. of sulphur) was ground up with crude rock-salt, moulded into bricks, dried, and calcined in a kiln. After three or four weeks the decomposition was

pretty complete; the burnt bricks were lixiviated, the liquor evaporated to dryness, the residue treated with sulphuric acid and heated strongly, in order to decompose ferric and aluminic chloride. A similar material was that remaining at Gouhenans (Haute-Saône) from the preparation of slaty coal for sale.

The process employed at Wallsend for some time was more similar to the original process of Longmaid, and distinct from it chiefly by the furnace (sketched in figs. 7 and 8). The rever-

Fig. 7.

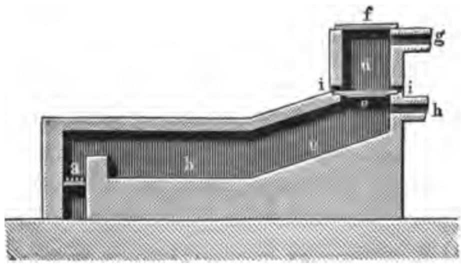
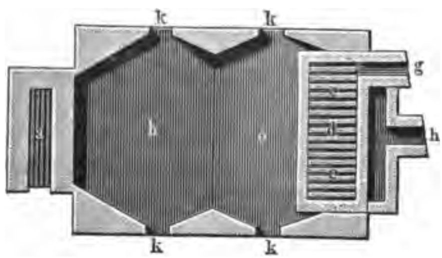


Fig. 8.



beratory furnace, heated by a fire-place, *a*, has only two beds, *b* and *c*, of which *b* is horizontal, *c* rising towards the back; above the back part of *c* rises the kiln *d*, whose grate-bars *e e* are easily movable in the openings *i i*; on the top it is closed by the lid *f*, used for charging. *g* is a flue leading from the kiln; *h* another, leading from the furnace to the chimney; both provided with dampers. The openings *i i* also serve for admitting and regulating the air; this can also be done from the working-doors *k k*. The fresh mixture is first charged through *f* into the kiln *d*; then, when the charge has been withdrawn from *b* and that from *c* has been moved forward on to *b*, the grates *e e* are drawn out and the con-

tents of *d* dropped into *c*; then the grates are put in again, and *d* is charged anew. Usually the fire-gas travels from the interior of the furnace through the kiln *d*, and from this through *g* to the chimney; but if the heat becomes too great, the dampers are so placed that a portion of the fire-gas is conveyed away by *h*.

Longmaid's process has, it is true, not been able to compete with the usual one, both on account of the above-mentioned incompleteness of the decomposition, which necessitates a treatment with sulphuric acid, and owing to the necessity of lixiviating the product of calcination and consuming fuel for making anhydrous sulphate. It has consequently been given up for some time; but it has given an impulse to two important processes—of which one, copper-extraction by calcining with salt, has become an established working process, and the other, the preparation of sulphate by roasting the pyrites apart from the salt, and thus doing away with the lixiviation, in the hands of Hargreaves and Robinson promises to do the same thing.

Similar plans have been proposed by Carny, and by Mesdach (French patent, 1858; Wagner's Jahresb. 1858, p. 118). The latter conducts the gas generated in a separate roasting of pyrites over moistened common salt; the SO_2 is used to decompose water, and the freed oxygen to cause the formation of sulphate from NaCl and SO_2. This process was a precursor of Hargreaves's, though exhibiting a very imperfect comprehension of its principles. Also by Thibierge (Dingl. Journ. clxx. p. 312), who mixes 300 parts of peat, 300 pyrites, and 65 common salt, and obtains a yield of 162 sulphate [?].

Robb (English patents of March 26th and April 2nd, 1853), who, as already mentioned (Vol. I. p. 641), proposed to make sulphuric acid by conducting burner-gas over red-hot ferric oxide, proposed to make sulphate by conducting sulphurous acid over a faintly red-hot mixture of common salt and ferric oxide, or, in lieu of the latter, pyrites, manganese, &c., shaped into balls or bricks by the help of clay. If steam is admitted, hydrochloric acid is formed—without air, free chlorine. Robb thus already, before Mesdach, separated the burning of pyrites from the employment of SO_2; but he retained the greatest drawback, viz. the mixing of the salt with the other materials, which necessitates lixiviation. He can thus only be called one of Hargreaves's precursors.

Weldon, on 5th February, 1872, patented the manufacture of

sulphate by heating NaCl with *manganese sulphide,* along with air, or with air and steam together,—also from NaCl along with Mn_2O_3 and CuO or Fe_2O_3 in a current of SO_2 and air, also with steam —or in a current of SO_3, or of CO—in short, a large number of combinations, none of which seems to have found any practical application.

According to a patent taken out by Hutchinson (January 1st, 1876), a finely powdered mixture of alkaline chlorides and metallic sulphides or brimstone is dropped down in a tower or revolving cylinder, whilst a red-hot mixture of air and steam traverses it; or the chlorides are to be dropped by themselves as a rain, and brought into contact with the gas from burning the metallic sulphurets by themselves, mixed with air and steam. This is especially recommended for the gas from metallurgical operations, which is otherwise lost. The first proposal would agree with Longmaid's, the second with Hargreaves's process, with this difference—that the substances are brought into contact with red-hot gas in the shape of a rain of dust. The escaping muriatic acid, mixed with chlorine, is to be utilized in the usual way. This process seems to offer unsurmountable practical difficulties, and will hardly come into operation for the manufacture of sulphate.

4. *From common salt and Epsom salts.*—Scheele already in 1787 observed that, if solutions of magnesium sulphate and sodium chloride are mixed and the solution cooled down at least to −3° C., Glauber's salt crystallizes out and magnesium chloride remains in the mother-liquor (Wagner, 'Regesten der Sodafabrikation,' p. 25). But probably the previously mentioned "Friedrichsalz," sent out from the Friedrichshall salt-works since 1767, was made in the same way, of course without any understanding of the process. We have also already mentioned the application of the same reaction to the mother-liquors of the salt-gardens in the South of France, and to the residue from dissolving the potash salts at Stassfurt. As a real principal product, Ramon de Luna (Wagner's Jahresb. 1855, p. 59) proposed to make sodium sulphate from the Epsom salt found in several parts of Spain, especially near Madrid. An intimate mixture of 2 parts of crystallized or 1¼ part of slightly dried Epsom salt and 1 part of common salt is to be brought to a red heat: hydrochloric acid escapes; and the residue consists of a mixture of sodium sulphate and magnesia. If this is treated with water at 90° C., sodium sulphate, with any undecomposed magnesium sulphate, is dissolved;

the latter is converted by milk of lime into calcium sulphate and magnesia, and thus removed. De Luna in this way prepared 12 tons of Glauber's salt; but he has had no successor.

Long before him Lord Dundonald had used the same plan. In his patent of Feb. 28th, 1795, he proposes to make Glauber's salt by mixing sea-salt or rock-salt with the sulphate of alumina, iron, or magnesia (expressly mentioned as "Epsom salts"), or with gypsum, all in solution or otherwise, adding to this a suitable quantity of clay, preferably containing iron, drying, grinding, and heating in a reverberatory furnace, crucible, or the like, till the muriatic acid is driven off. After this the Glauber's salt is to be extracted by lixiviating and washing, and to be obtained by crystallization or evaporation to dryness. Epsom salt and rock-salt ignited together yield the product even without addition of clay containing iron, but not so completely.

Margueritte in 1855 obtained a patent for the *indirect* preparation of sodium sulphate from magnesium sulphate by the mediation of lead sulphate—which will be mentioned again further on, as well as Anthon's process introducing gypsum.

5. *From common salt and calcium sulphate.*—Lord Dundonald's proposal of this kind has been just mentioned. The next proposal of the same kind is stated, in Wagner's 'Regesten,' p. 29, to have been made by Hodson; but no such patent appears in the English list, and there may possibly be a confusion with Wilson, who on November 22nd, 1838, took out a patent, in which it is prescribed to boil together common salt, gypsum, and magnesium carbonate by steam in certain proportions. Calcium carbonate is formed; and from the solution, on concentration, anhydrous sodium sulphate is separated; magnesium chloride remains in solution. The magnesia is precipitated by lime, and reconverted into carbonate by a current of carbonic acid. Tilghman (patent of Feb. 1st, 1847), among many other things, also proposed to bring equal parts of common salt and gypsum to a red heat in fireclay cylinders lined with magnesite, and to conduct superheated steam over the mixture; the escaping muriatic acid gas is condensed, and the residue worked up by lixiviation. This process has never been carried out on a large scale; and it could not succeed, as Knapp found (Liebig's 'Jahresbericht,' 1847–48, p. 1054) that the commencement of decomposition could be observed in a glass tube, but not in a gun-

barrel—according to which, in Tilghman's process silica seems to play a part.

That on melting together common salt and gypsum no decomposition takes place, has been shown by Trommsdorff (Gmelin-Kraut's 'Handbuch der Chemie,' 5th ed. ii. p. 185), Karsten (Wagner's 'Regesten,' p. 29), and H. L. Buff ('Dingler's Journal,' clxxii. p. 282). Greenshields (patent of December 22nd, 1852) states that by adding powdered coal or coke, igniting and lixiviating, not pure sulphate, but a product containing much sodium sulphide, is obtained, which was to be worked up with small coal and calcium carbonate in an ordinary black-ash furnace.

Nicklès (Répert. de Chim. appl. 1862, p. 464) ignites a mixture of anhydrite, rock-salt, and manganese. From the rock-salt the oxygen of the manganese liberates chlorine, which escapes in a gaseous form, whilst sodium sulphate and lime remain behind. In this process, however, at most 15 per cent. of sodium sulphate can be obtained; also the volatility of sodium chloride at a red heat is inconvenient for this and any similar processes.

Anthon ('Dingler's Journal,' clxxi. p. 138) obtained an Austrian patent for the following process. It is based on the fact that magnesium carbonate is completely decomposed by calcium sulphate, magnesium sulphate and calcium carbonate being formed, and the other fact that common salt and magnesium sulphate yield sodium sulphate and magnesium chloride. Equivalent proportions of common salt, calcium sulphate, and burnt magnesia are mixed with a weight of water from 6 to 8 times that of the common salt; and, with constant agitation, carbonic acid is passed through up to saturation; the solution is separated from the calcium carbonate formed, and evaporated, whereupon Glauber's salt crystallizes out, and magnesium chloride remains in the mother-liquor. Or magnesium carbonate is employed from the first, and the mixture stirred for three or four hours. The magnesia is to be obtained by burning magnesite or dolomite, by precipitating magnesium chloride with lime, or by sufficient heating of magnesium chloride.

Another indirect method of preparing sulphate from gypsum was patented in Bavaria by Bandiner in 1832 (Wagner's Jahresb. 1858, p. 102); it has been proposed again by Fleck (Fabrik. chem. Prod. aus thier. Abfällen, p. 131) and Reinsch (Wagner's Jahresb. 1870, p. 167), and consists in converting finely powdered gypsum

by means of ammonium sesquicarbonate into ammonium sulphate, and preparing from the latter, by sublimation with common salt, sodium sulphate and sal-ammoniac.

6. *From common salt and ammonium sulphate.*—This process, in which sal-ammoniac is the principal object and sodium sulphate only a by-product, has been already mentioned. The process has been employed since 1795 at Grenelle in France, later on by Prückner, Persoz, Poole, and others, and is still in common use. One equivalent of ammonium sulphate and two of common salt are dissolved in warm water and evaporated, so that anhydrous sodium sulphate is separated. When the liquid is concentrated up to the point that a drop solidifies on cooling, it is run off; on cooling, sal-ammoniac crystallizes out. The proposal of Bandiner, mentioned in No. 5, belongs to this class as well.

7. *From common salt and aluminium sulphate or alum.*—This process has been already mentioned, where sodium sulphate is a by-product; as principal product it was made about 1750 by Constantin at Welle, near Osnabrück, from alum (Wagner's 'Regesten,' p. 33), and by Lord Dundonald in 1795 from aluminium sulphate (see above). The same decomposition has been again carried out (according to Wagner's 'Regesten') by Gren, S. Hahnemann, Fuchs, Piepenbrinck, and Tuhten; Pelouze and Kuhlmann's patent of 1850 and Cunningham's patent of 1850 also belong to this class. In this process the object is either the preparation of alumina,

$$Al_2(SO_4)_3 + 6\,NaCl + 3\,H_2O = 3\,Na_2SO_4 + Al_2O_3 + 6\,HCl,$$

or that of aluminium chloride,

$$Al_2(SO_4)_3 + 6\,NaCl = 3\,Na_2SO_4 + Al_2Cl_6.$$

Since most alum is not made from aluminous schist, but from sulphuric acid and clay, such a preparation of sodium sulphate cannot take place any more as a principal product, but only as a by-product in making aluminium chloride for dyers &c.

8. *From common salt and ferrous sulphate or other iron salts.*—That sodium sulphate can be obtained from ferrous sulphate and common salt, both by igniting them together and by mixing the solutions of both salts and exposing to the cold of winter, has been known long since. The former process was described in 1789 by S. Hahnemann, the latter by H. van der Ballen, Lieblein, Tuhten,

and Wiegleb (Wagner's 'Regesten,' p. 30); Lord Dundonald, in 1795, likewise mentions it. Athenas, in 1793, already had an alkali-works in Paris founded upon this. Wilson, on November 22nd, 1838, patented the addition of common salt to a boiling solution of ferrous sulphate, whereupon anhydrous sodium sulphate is precipitated and washed with a hot saturated solution of common salt, in order to remove the mother-liquor of ferrous chloride. He further converts the latter into ferrous hydrate, and by means of this prepares sodium hydrate.

According to Berzelius ('Lehrbuch der Chemie,' 4th ed. iv. p. 153), at Fahlun sodium sulphate is obtained from the pit-water and from the mother-liquor got in making copperas, by mixing them with the proper quantity of common salt, evaporating to dryness, and igniting. The pit-water contains several sulphates, especially those of iron, which on igniting decompose the sodium chloride to form sulphate, whilst metallic chlorides are formed and partially volatilized; partially they give up chlorine and take up oxygen from the air. The calcined salts are dissolved in boiling water, and a crop of sodium sulphate crystals obtained on cooling. Abich introduced the same process at Schöningen, and employed the ferrous chloride remaining in solution for making Prussian blue (Mitscherlich, Lehrb. d. Chemie, 1847, ii. p. 58). Already in 1819 the same thing exactly is described in a patent of Fuller's. In spite of all this the process was described as new in 1852 by E. Thomas, Delesse, and Boucard (Wagner, *l. c.*).

Macfarlane ('Silliman's Journal' (2), xxxvi. p. 269) ignites dried copperas and common salt in a current of air. At first ferric chloride is formed; and this yields ferric oxide and chlorine; so that the residue contains sodium sulphate and ferric oxide. An addition of ferric oxide assists the reaction by making the mass more porous and less fusible. 828 parts of copperas are dried in a gentle heat and partly oxidized, intimately mixed with 352 parts of sea-salt and 78 parts of ferric oxide, brought to a low red heat in a muffle furnace, and a current of air dried by caustic lime is conducted over the mixture. The temperature should not be so high that ferric chloride can sublime; the mass must be stirred from time to time. In this case only chlorine escapes, mixed with nitrogen:

$$2\,FeSO_4 + 4\,NaCl + O_3 = 2\,SO_4Na_2 + Fe_2O_3 + Cl_4.$$

In the muffle there remains a mixture of ferric oxide and sodium sulphate, which is, without lixiviation, converted into caustic soda and iron sulphide by a process to be described in the Third Book. Even this process, where lixiviation is avoided, does not pay.

Persoz and Kuhlmann (Dingl. Journ. cxxxiv. p. 394) in 1850 obtained a patent for decomposing common salt by alum-mud, basic ferric sulphate, or calcined alum-slate—that is to say, essentially the same materials as the last, only already partially oxidized. They also introduce steam during the heating; so that the reaction will be

$$Fe_2(SO_4)_3+6\,NaCl+3\,H_2O=3\,Na_2SO_4+Fe_2O_3+6\,HCl.$$

The residue is to be separated by lixiviation.

It will be seen that the process employing ferrous or ferric sulphate in the dry way is a transition to calcining pyrites with common salt (usually called Longmaid's process); the latter is anyhow preferable, because in this case the ferrous sulphate is not prepared by itself, but employed at once in the nascent state.

9. *Common salt and cupric sulphate* (Wilson, 1838; Hunt, Jan. 21st, 1840).

10. *Common salt and zinc sulphate* (Hunt, 1840; Boulton, Feb. 23rd, 1852; Kessler in Wagner's Jahresb. 1859, p. 244).—In both cases the process is essentially the same as that of Wilson, described above for ferrous sulphate; only the mother-liquors of cupric or zinc chloride are precipitated by lime, and the oxides worked up in various manners. Here the manufacture of sodium sulphate as principal product is out of the question. To this class belongs the manufacture of sodium sulphate from the mother-liquors of the wet copper-extraction.

11. *From common salt and manganese sulphate.*—Barrow (patent, Feb. 26th, 1856) describes this process, which is quite analogous to the former ones, as part of a very unpractical and complicated new process for manufacturing alkali.

12. *From common salt and lead sulphate.*—Margueritte in 1855 patented the following process:—Equivalent proportions of lead sulphate (obtained by calcining galena) and common salt are mixed, and the mixture heated for a long time in retorts or open roasters up to a bright red heat. Sodium sulphate and lead chloride are formed; the latter is volatilized, and condensed in a suit-

able apparatus. The residue contains undecomposed lead sulphate and sodium sulphate, which are separated by dissolving and evaporating; the lead chloride is again converted into sulphate by means of gypsum or Epsom salt; and it is therefore the latter that furnishes the sulphuric acid, not the lead sulphate, which only serves as carrier. The reactions are :—

$$\text{I. } 2NaCl + PbSO_4 = Na_2SO_4 + PbCl_2;$$
$$\text{II. } PbCl_2 + \underset{(\text{or } CaSO_4)}{MgSO_4} = PbSO_4 + \underset{(\text{or } CaCl_2)}{MgCl_2}.$$

This process was described in detail in 'Dingler's Journal,' clviii. p. 298; it has never been carried out on an industrial scale, in which a complete condensation of lead chloride and the avoidance of other losses of lead could certainly not be expected.

CHAPTER III.

SULPHATE AND HYDROCHLORIC ACID FROM COMMON SALT AND SULPHURIC ACID.

This is not merely the process which up to this day furnishes the largest portion of all the sulphate, but at the same time the oldest, viz. that employed by Glauber himself. He and his successors obtained sulphate in the first instance as a by-product in making hydrochloric acid in glass retorts. But when the manufacture of artificial soda, at the end of the last century, received a sudden impetus from certain circumstances to be explained in the Third Book, that of sulphate had to be increased in the same proportion; and the time came when, on the contrary, muriatic acid became a by-product, and in many cases was altogether lost—a state of matters which in some places exists to this day. Leblanc himself prepared the sulphate which served as a starting-point for his soda-process by decomposing common salt with sulphuric acid.

At the same time, of course, the apparatus had to receive another shape—at first that of iron cylinders when the muriatic acid had to be condensed, or of open lead dishes when this was not the case; the latter were frequently heated by the waste fire of the soda-furnaces, and were usually in connexion with a calcining-furnace. But only when the alkali-manufacture had gained a firm footing in England, and began to be carried on there on a much larger scale than on the Continent, were apparatus adopted suitable for producing large quantities. The first who in England made sulphate by decomposing common salt with sulphuric acid was William Losh, who had studied chemistry in France, and, having returned to his native country in the beginning of this century, erected a chemical works at Walker-on-Tyne. A weak-brine spring existing there first gave occasion to this. In 1812 or

1815 lead chambers were erected, the product of which was partly sold as oil of vitriol, partly employed for decomposing common salt obtained from various sources. The first furnaces for this purpose were made of lead and lined with bricks; 2 cwt. of salt was introduced at a time; and the vitriol was slowly poured in from a carboy through a hole in the furnace-roof. The muriatic acid escaped into the air by a short chimney. After three hours a plug in the side of the lead pan was drawn out and the semi-liquid mass was run into a lead vessel, where it solidified into a hard cake, which was broken up and calcined to finished sulphate. The lead furnace, which stood a very short time, was in 1828 replaced by a brick furnace, and in 1840 by cast-iron decomposing-pans, such as are now used, both by Lee at Felling-on-Tyne and by Gamble at St. Helens (Clapham, 'Soda-Manufacture on the Tyne,' p. 14). A second factory of a similar kind arose at Blyth in 1822; but 1823 was the real year of birth of the manufacture of sulphate (and soda) on a large scale—when the enormous salt-duty was taken off, which had prevented any great extension. In that year James Muspratt erected a factory at Liverpool, in which common salt was decomposed with sulphuric acid, and Leblanc's process was carried out completely. In the same year Cookson & Co. (now the Jarrow Chemical Company), at South Shields, followed suit, perhaps even before Muspratt; and in 1827 a number of works arose both in Lancashire and on the Tyne.

The following will give an idea of the present extension of this trade:—In 1869 there were decomposed in England 326,000 tons of salt; in 1676, 647,000 tons in the United Kingdom.

Excepting very few cases, viz. the cylinder furnaces of the oldest and the mechanical furnaces of the most recent time, *the operation of making sulphate* consists of *two stages.* The common salt is at once brought together with the whole quantity of sulphuric acid required—that is, 1 SO_4H_2 to 2 NaCl, which ought to yield simply Na_2SO_4 and 2 HCl; but, owing to the tendency of sulphuric acid to form acid salts, the decomposition only proceeds in stages. The usual representation of the process is, that at first the following reaction takes place—

$$\text{I. } \underset{\text{Common salt.}}{NaCl} + \underset{\text{Sulphuric acid.}}{H_2SO_4} = \underset{\text{Acid sodium sulphate.}}{NaHSO_4} + \underset{\text{Hydrochloric acid.}}{HCl},\text{—}$$

and that then a second molecule of common salt comes into play, and the following reaction sets in—

II.	$NaHSO_4$	+	$NaCl$	=	Na_2SO_4	+	HCl.
	Acid sodium sulphate.		Common salt.		Sodium sulphate.		Hydrochloric acid.

These two reactions, however, certainly are not sharply separated; and only so much can be said, that, on the whole, at a comparatively low temperature sulphuric acid and common salt, even when the latter is in excess, act upon each other *principally* according to the first equation, whilst at a higher temperature the excess of common salt acts upon the acid sodium sulphate according to the second equation—in other words, that the decomposition of common salt becomes *perfect* only at a higher temperature, viz. at a pretty strong red heat. The two stages of work mostly employed in practice do not coincide with the above equations; for whilst, on H_2SO_4 meeting $2NaCl$, according to the first eqnation only 50 per cent. of all the hydrochloric acid ought to be given off, in the *technical* first stage, the decomposing-pan, 66 to 70 per cent. of all the HCl are given off, although nothing like a red heat is attained there.

Thus by the action of liquid sulphuric acid on solid common salt there is always formed, first, sodium sulphate (whether acid or neutral), which is solid, and, secondly, hydrochloric acid, which escapes as a gas and has to be condensed into a liquid, at the same time with aqueous vapour coming from the water always present in sulphuric acid. The strongest sulphuric acid is never employed, but acid of at most 144° Tw. = 78 or 80 per cent. SO_4H_2 and 22 to 20 per cent. of H_2O. The common salt also contains more or less water. The *water* is mostly not given off in the first stage of the operation (that is, in the pan), but in the second (the calcining-furnace or roaster); with dilute sulphuric acid, however, a good deal of water must already be driven off in the pan. As steam on being condensed to liquid water gives out a good deal of heat, and as cooling is just one of the principal conditions of effectual condensation of muriatic acid, the latter is much more difficult when dilute sulphuric acid has been employed for decomposing the salt.

The important part played by the *air* mixed with the HCl and the steam will be explained hereafter.

At present we need only remember that, along with the preparation of sodium sulphate, the *condensation of hydrochloric acid* must always take place; in most cases, though not in all, the condensed muriatic acid can be sold, or used by the manufacturer himself.

If *hydrochloric acid is the principal product*, a different style of work is adopted—not, however, that sometimes mentioned, of taking more than 1 SO_4H_2 to 2NaCl, but, inversely, that of taking *less* sulphuric acid than required by theory. In the former case certainly all the hydrochloric acid would be completely expelled; but it would be contaminated by sulphuric acid escaping at the same time. In the second case, certainly, a little common salt remains undecomposed; but the hydrochloric acid will be quite free from sulphuric acid; and as probably everywhere sulphuric acid is by far the dearest of the two ingredients, an excess of common salt will be employed if the value of the hydrochloric acid is the principal thing and that of the residue of (impure) sodium sulphate only a secondary consideration. This is the case in all places where, owing to the high price of coals, the consumption of sulphate for making glass or alkali is excluded, but where hydrochloric acid is required for other purposes, whilst its transit from the centres of chemical industry is extremely dear, making its local production as a principal matter remunerative.

The raw materials of the manufacture of sulphate are the following:—first, *sodium chloride* with more or less of impurities, as common salt or rock-salt; secondly, *sulphuric acid*; thirdly, in many cases products containing partly sulphate, partly either free salt or free acid (residues from the manufacture of muriatic acid in cylinders and from that of nitric acid, the pan-scale of salt-works &c.). (The "saltpetre-salt" obtained in making nitrate of potash from potassium chloride and nitrate of soda is, owing to a percentage of 0·5 of saltpetre, unfit for making sulphate; it strongly acts upon the pans, tools, &c., and the hydrochloric acid contains chlorine.) The materials mentioned in the third place always play a secondary part, and are nearly always used only as an addition to common salt, with a corresponding change in the addition of sulphuric acid. Thus common salt and sulphuric acid remain as the proper raw materials for the sulphate-manufacture.

I. *Common salt.* It is not indifferent in which form the salt is employed. Most suitable for sulphate is the common pan-salt,

especially that obtained by fishing below the boiling-point of the brine, which is of coarse grain, not the fine salt obtained by evaporation at a boiling heat, called "butter-salt." Still less adapted for sulphate-making is rock-salt; this must under no circumstances be finely ground, but only crushed to a coarse powder. The reason is that the salt should possess some porosity in order to dissolve readily in the sulphuric acid; this most easily and quickly takes place with coarse-grained pan-salt—its loose, rough crystals presenting a large surface to the attack of the acid, and spaces for absorbing it. The conditions are less favourable with coarsely crushed rock-salt, which equally admits the acid into its interstices. but is much less easily quickly dissolved, owing to its glass-like surface. The worst case is that of finely ground rock-salt or butter-salt. Here the particles of salt lie so closely together that the acid penetrates into them with difficulty; and, in spite of the much larger surface actually presented by the salt in this form, the attack of the acid is, for the above reason, much slower. Only by constant stirring can this drawback be met; and it can never be entirely overcome. The salt lies dead on the bottom of the pan, cakes together, and easily causes the pan to crack. This fine-grained salt also obstinately adheres to the tools, and from this cause is difficult to work.

The chemical properties of the salt are also of great importance. Of course it is all the more fit for sulphate-making the purer it is—that is, freer from gypsum (anhydrite), magnesium chloride, ferric oxide, clay, &c. In this respect the common pan-salt has a considerable advantage over rock-salt, which is certainly not compensated by its larger percentage of water; and from this cause the British works are already a good deal in advance of most of the continental works, because they can obtain the beautiful white, pure Cheshire salt at a price below that of rock-salt everywhere except close to the mines, whilst its value for sulphate-making is much greater than that of rock-salt. The calcium sulphate especially, in rock-salt sometimes amounting to 8 per cent., is very troublesome, because it gets into the sulphate and produces bad soda-ash. Magnesium chloride and calcium chloride consume sulphuric acid and thus cause a loss; but they occur only to a slight extent in all kinds of salt. Very troublesome are ferric oxide and alumina, even in sulphate not intended for glass- but for alkali-making; for this reason the Cheshire rock-salt is never

employed for sulphate. Water has not to be reckoned as an im purity; but if present in excess, it makes the condensation mor difficult; and it is disagreeable also because the salt dries in th warehouse, and consequently the proportion of acid required fo decomposing it has constantly to be determined again.

Sodium chloride, NaCl, consists of 23 Na and 35·46 Cl, or o 39·34 per cent. Na and 60·66 per cent. Cl. Its hardness is 2·5 its spec. grav. 2·1–2·257. It melts at a low red heat—accordin to Carnelly (Journ. Chem. Soc. 1878, ii. p. 280) at 772° C.; at a higher temperature it is volatilized. It crystallizes in cubes below −10° C. in large hexagonal plates, of the compositio $NaCl+4H_2O$, which above −10° C. quickly fall into small cubic crystals of common salt and a saturated solution of the same 100 parts of water, according to Poggiale, at 0° C. dissolve 35·52 at 109°·7 C. 40·35 parts of sodium chloride. In spirit of wine it is very slightly soluble.

The deposits and the manufacture of salt form a very importan chapter in chemical technology, which, however, is beyond the scope of this treatise; we shall only quote the analyses of some important descriptions of salt employed in alkali-manufacture. (See Table opposite.)

It will also be interesting to mention the *prices* of salt in different places. According to Mactear (Reports &c. p. 4), the price of salt in Scotland in 1798 was about £3 10*s*. per ton, to which £3 was added for duty; and in the same year the duty was raised by £13, so that the price of salt rose to £19 10*s*. In 1805 the duty in Scotland was £12, in England £30 per ton! In 1829, after the duty had been taken off, the price of salt in Scotland was only 22*s*., in 1869 only 14*s*. 6*d*. per ton. At Newcastle-on-Tyne salt bears the same or a slightly higher price, as it comes exclusively from Cheshire; at the Lancashire works it only costs about 6*s*. to 8*s*. per ton.

Rock-salt at Stassfurt costs about 3*s*. per ton; but railway-transit makes it much dearer for the chemical works, so that on the Rhine it costs 15*s*. to 16*s*. Common salt costs at the salt-works in Würtemberg 15*s*., in Saxony 17*s*. to 28*s*. per ton.

II. The *sulphuric acid* used for sulphate-making is always the common chamber-acid, or as it is obtained by evaporation in lead pans or in the Glover tower. Such of its impurities as usually occur do no harm in the manufacture of sulphate; only, for the sulphate destined for glass-making, acid containing iron should be avoided. The arsenic contained in the sulphuric acid does not

remain with the sulphate, but passes over into the muriatic acid, and certainly in this may sometimes be inconvenient. Nitrogen compounds and lead in ordinary vitriol occur in too small quantities to do any harm.

Of greater importance is the *concentration* of the sulphuric acid employed. The best strength is from 140° to 144° Tw. Stronger acid, even if it can be obtained without any further expense (for instance, by a Glover tower), is not good for the process, because the hydrochloric acid is given off too vehemently and the mass solidifies too quickly, before it has been thoroughly mixed and decomposed. The drawback of too great concentration is certainly easily remedied by adding chamber-acid, as at the factories working with a Glover tower is regularly done. But the opposite drawback of too much dilution is not so easily avoided in the absence of a Glover tower and if it is too expensive to concentrate in lead pans. Certainly no expenditure should be needed for this, as the chamber-acid can be evaporated up to 144° Tw. on the top of the pyrites-burners. But before this was well known, at many works, to avoid the expense of concentration by separate fuel, the chamber-acid was taken directly for the decomposing. So long as its strength is not below 128°, or, *at least*, 124° Tw., no great harm is done; only the work is slower and the condensed muriatic acid rather weaker. But those manufacturers who do not get the chamber-acid up to at least 124° Tw., ought not to shirk the expense of concentration, even if they possess no pans on the burners or no Glover tower; for weaker acid not only retards the operation very much, makes the condensation more difficult, and yields weaker muriatic acid, but it also causes great wear and tear of the decomposing-pans. This case easily occurs in starting works before the apparatus are in proper working order; for days or even for weeks they must sometimes work with acid of, say, 106° Tw.; but such a proceeding is generally paid for by a quick destruction of the decomposing-pans.

Apparatus for manufacturing Sulphate of Soda and Muriatic Acid.

Although in some cases the manufacture of sulphate is the secondary, and that of hydrochloric acid the primary object, we shall here describe all the apparatus for both purposes.

1. *Manufacture in glass retorts.*—This only takes place in a few localities, where glass is cheap and muriatic acid very dear; for only in the latter case are glass retorts used. This process has the

advantage of supplying muriatic acid quite free from iron. Figs. 9 & 10 (from Payen's 'Précis,' i. p. 415) show this arrangement.

Fig. 9.

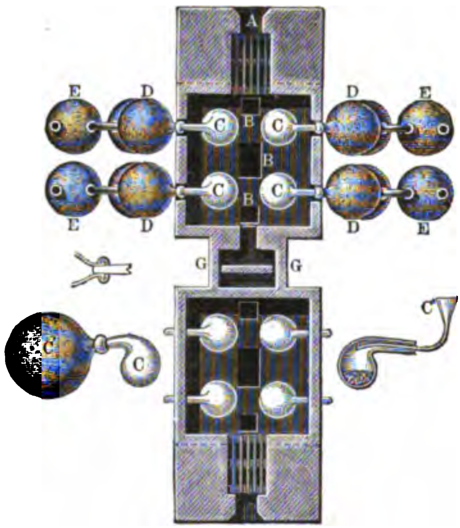
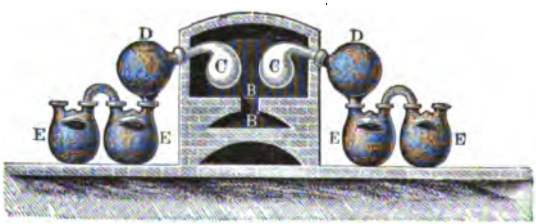


Fig. 10.

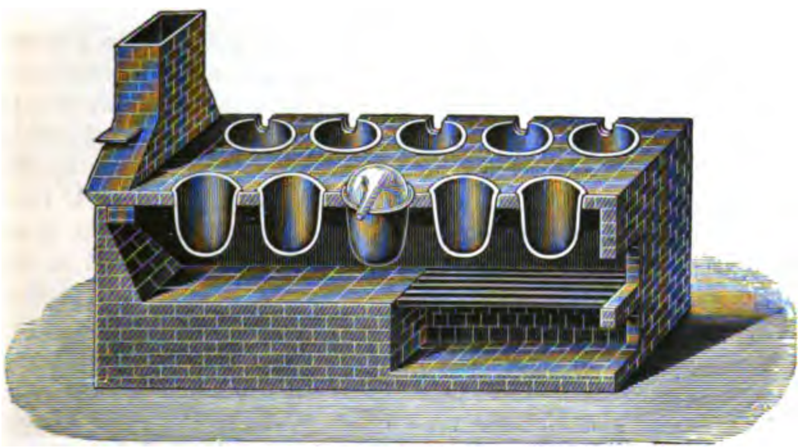


The fire from A passes through the flue B′ and the holes B, surrounds the retorts C, the necks of which either (as at C′) enter directly into glass receivers, or (as shown at D) first into a tubulated glass ball, from which the acid flows into the Woulfe's bottles E E (usually three), in which the vapours are completely condensed. Here the acid is also separated according to its degree of purity: the first bottle does not receive any water; and this contains the more impure acid; the second and third are charged with water, and contain purer acid. The salt is filled into the retorts, after

their necks have been turned upwards; then they are turned sideways; and C'' shows how the sulphuric acid is poured in by means of a funnel continued into a long bent tube; the receivers are put on at once, having been charged with six equivalents of water for each equivalent of common salt, and the fire is lighted.

The arrangement shown in the diagrams contains four retorts in each furnace, and has two furnaces leading into a common flue with a short partition-wall for keeping off false draughts. Each of the retorts is protected from the direct action of the fire by a loose brick wall which is taken away after each operation. In Germany, when this style of work was still carried on, galley furnaces, as shown in fig. 11, were preferred, in which the retorts were heated

Fig. 11.



in sand-baths or over the free fire, but in this case protected by a coating of clay.

Since on employing the same number of equivalents of salt and of sulphuric acid a difficultly fusible residue of neutral sulphate remains in the retorts, which causes them to crack on cooling, there must be much more sulphuric acid (about three times the equivalent of the salt) put into the retorts, if they are to be used several times; the contents are then poured out in the liquid state. In this case there is great danger of getting an acid very much contaminated with sulphuric acid. When the process was actually in use, the retorts were mostly broken in order to obtain

the sulphate, and the broken glass melted up and worked into retorts in neighbouring glass-works.

2. *Manufacture in cast-iron retorts* (cylinders).—This also only takes place where muriatic acid is the principal product; it admits of a considerably larger scale of working than glass retorts. Figs. 12 to 18 show such an arrangement, also from Payen's 'Précis.' Two cylinders A A lie in a furnace, of which usually a larger number are placed side by side. B is the fireplace, C the partition-wall between, D the fire-arch; *e e* the escape-holes leading to the flues *f* and *g* which open into a chimney common to all the furnaces. The back end of the cylinders is either closed by a cast-metal plate or by a wall of bricks with very narrow joints, set in mortar of 1 part of plastic clay and 1 part of burnt fireclay. [This latter arrangement will certainly not stand the action of the melting mass; a round flag of stone or of stoneware in *one* piece is undoubtedly preferable.] This end of the retort contains a stoneware pipe *a*; on this is put a stoneware junction *j*; and this leads to the receivers I. The joints are plastered either with clay or with gypsum. The receivers are singly connected with a second row of receivers by the pipes K; the second row communicates by the pipes L L; at the end of the row there is a junction-pipe L′ for a third row of receivers, connected with a fourth row by the pipes L″ L″; a fifth and a sixth row (M N, O P) ultimately lead to the chimney H. This connexion, however, is bad; in the case of cylinders there is no necessity of producing an artificial draught in the apparatus, by which a large quantity of acid is carried away without condensation and creates a nuisance in the neighbourhood. The receivers should and must condense the acid gas so far that the gas can issue freely out of the last of them; otherwise no chimney, but a coke-tower, must be employed (see later on).

The front end of the cylinders is closed for each operation by a cast-iron cover with handle P, a little clay making the joint tight; an opening R, $2\frac{1}{2}$ inches wide, receives the funnel tube S for pouring in the acid, and is afterwards closed by a plug S′.

The operation is carried on as follows. The first row of receivers is left empty, the others are half filled with water; the empty row receives the acid contaminated by sulphuric acid and sulphate carried over mechanically. The cylinders, which are 2 ft. 2 in. in diameter and 5 ft. 6 in. long, are charged with 160 kil. of salt, the cover is put on and luted; 128 kil. sulphuric acid of 144° Tw. is

Fig. 12.

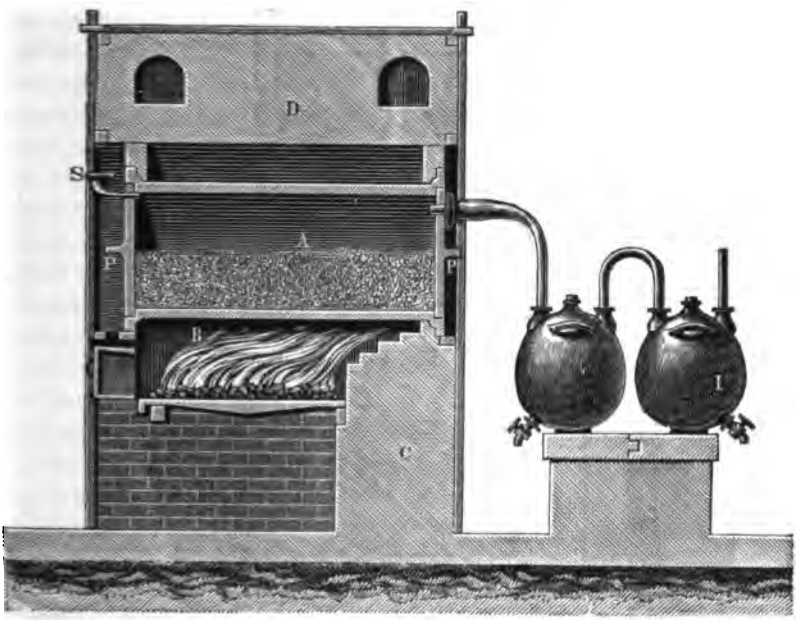


Fig. 13.

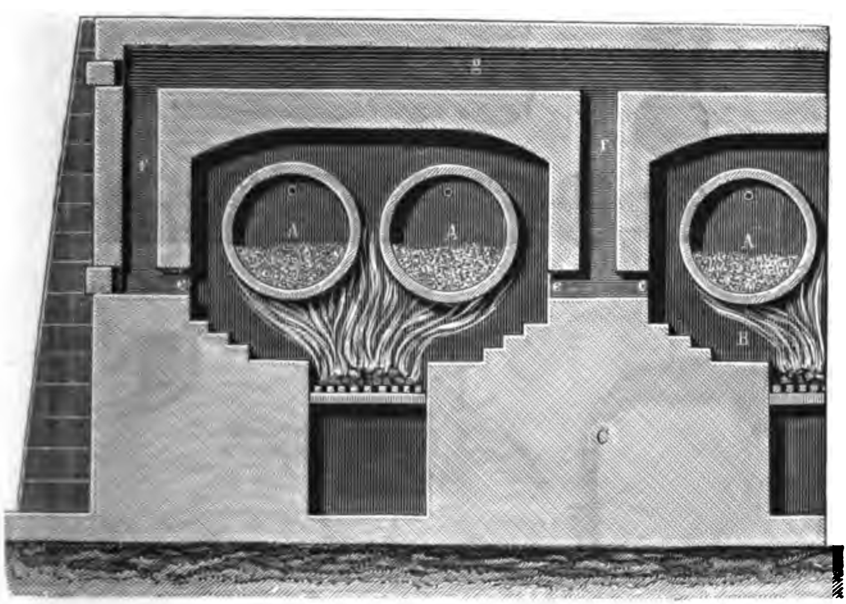


Fig. 14.

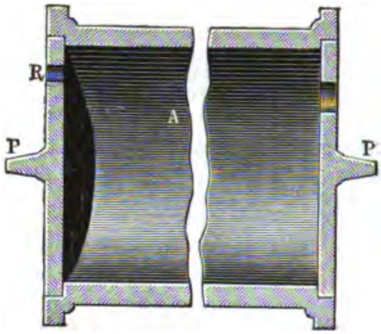


Fig. 15.

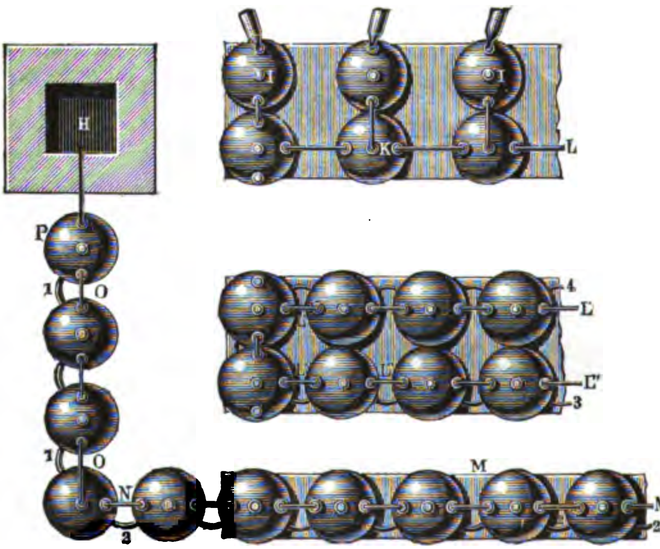


Fig. 16.

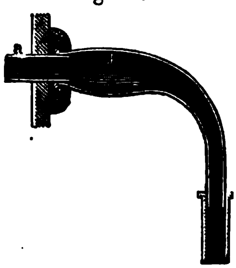


Fig. 17.

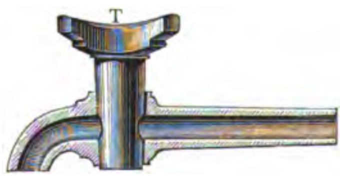
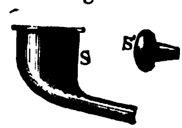


Fig. 18.



passed in through the funnel [this is considerably less than an equivalent of salt], the funnel taken out, the stopper put in. The reaction commences at once, and is assisted by a small, gradually increasing fire. The metal cylinders can easily be heated sufficiently for the conversion of the common salt into neutral sulphate; and therefore no more than an equivalent of sulphuric acid is employed, usually even less, because it is dearer than the salt and its loss of more consequence. The more dilute the sulphuric acid the more it acts upon the iron; and therefore it ought never to be below 152° Tw.; it will then evolve a good deal of muriatic acid while still cold, and the fire need only be applied later on.

The muriatic acid given off is condensed in Woulfe's bottles; according to the diagram, each of them has a tap, T, of its own; but this is not necessary, and it has become quite usual to connect the bottles with one another by elastic tubes or, still better, by overflow-pipes taking the acid from the bottom of one bottle to the middle of the next one, as we shall see hereafter.

In any case the gas travels in the direction K L L′ L″ M N O—that is, from the cylinders towards the chimney, whilst the water travels in the opposite direction, 1, 2, 3, 4; so that fresh water meets the gas almost free from acid, and the weak acid formed in this way is concentrated in the first rows of receivers by stronger gas. Altogether about 200 to 208 kil. of muriatic acid with about 40 per cent. [?] of dry HCl, showing 21° to 22° Baumé, are said to be obtained.

The completion of the operation is known by the fact of the gas-pipe becoming cold; the firing is then stopped, and the front cover is taken off by means of a hook put through the opening R. [There ought to be in any case, though Payen does not mention it, a set of pulleys, or at least a pulley provided with a chain and hook in such a way that it easily travels in front of each retort.] Then the cake of sulphate, weighing 180 to 184 kil., is raked out in one or two pieces. This is never pure sulphate, but either contains bisulphate, or, where the muriatic acid is the main thing, undecomposed salt; it can only be used for very common bottle-glass, and is therefore mostly worked up in alkali-works to good sulphate. It is usually called "cylinder-cake."

In France the cylinder furnaces seem to have been given up some time ago (comp. E. Kopp, in Wurtz's 'Diction. de Chimie,' ii. p. 1567); but in London and several other places they existed up to

the most recent time, in order to supply a local demand for muriatic acid. In many cases, however, the cylinders have been abandoned even where originally the muriatic acid was the chief product, and the less expensive plan of decomposing-pans has been adopted; the sulphate made in these, being a solid substance, can be sent to comparatively great distances; and any excess of muriatic acid over that saleable in the neighbourhood, such as is generally obtained on introducing the newer mode of manufacturing, can also be brought into a solid and saleable shape as bleaching-powder.

3. *Manufacture in furnaces.*—This is the only style in which sulphate has always been made on a large scale, where it is the principal product and muriatic acid only a by-product, often a very troublesome one.

The sulphate-furnaces, differently from the apparatus of glass or iron retorts described hitherto, always consist of two parts (leaving aside just now the mechanical furnace of Jones and Walsh), viz.:—one, consisting of cast iron or lead, in which the first stage of decomposition takes place at a lower temperature—the *decomposing-pan* or *pot*; and another, consisting of brickwork, in which the decomposition is completed at a higher temperature—the *roaster* or *drier*. Formerly, to be sure, the whole operation was sometimes carried out from beginning to end on the dished hearth of an open roaster, all hydrochloric acid escaping into the chimney along with the fire-gas; but this barbarous style of manufacture will not be described here at all. The *pan* in all cases is heated from the outside, although in some cases a further heating from the top is added; the *furnace*, however, is either an ordinary reverberatory furnace or open roaster, or it is heated partly by the direct flame and partly indirectly through the bottom (gas furnaces), or entirely by indirect heat (muffle furnaces or blind roasters).

The principal matters to be attended to in constructing a furnace are the following:—

(1) *The condensation of hydrochloric acid.*—The construction of the decomposing-apparatus varies according to whether the hydrochloric acid has to be more or less completely condensed, or, as now a practically complete condensation is always aimed at and possible, whether the object is that of obtaining the strongest acid for sale, or moderately strong acid for own use, or only weak acid for running away. Only in the last case, where nothing but very weak acid need be got, can pans worked by an open fire be em-

ployed; where acid is to be made for own use, the calciner may be either a close or an open roaster; but where sale-acid has to be made, close roasters are nearly always preferred. The reason of this difference is quite obvious, viz. that the muriatic acid can be made all the stronger in the condensing-apparatus, the less it is mixed with air and fire-gas.

(2) *Turning out large quantities*, with the largest possible saving of time and wages. In smaller works contrivances may be used which are out of place in large works, where very large quantities have to be turned out, and inversely. Thus, for instance, more work can be done with open roasters than with close ones, and most of all with furnaces where the pans are equally heated from above by the open flame, though in the latter case only weak acid can be obtained. The heating of the pan by the waste heat of the roaster is also, at least in England, principally confined to smaller works; in larger ones this is not generally done, because it makes one part of the apparatus dependent upon the other, so that they must frequently wait for one another, and nothing like as much work can be turned out in the same time as with separate fires. The extent of production, of course, must also determine the size of the furnaces and pans and even the material of the latter; in cast-iron pans much more work can be done than in lead pans, because they can be used much more roughly and fired more intensely. The largest production is possible in the mechanical furnaces.

(3) *The consumption of fuel.*—Where fuel is dear and wages low, opposite considerations prevail to those stated just now for large production. The furnaces are then constructed so as to consume as little fuel as possible; the pan is always heated by the waste fire of the roaster, sometimes even both by the waste heat of a black-ash furnace, but with this result, that much less work can be done in a furnace during a given time.

(4) *The purity of the sulphate.*—Where the object is that of making sulphate for glass-works, as free from iron as possible, lead pans are even now used, as prescribed by Leblanc. Thus in Belgium, for instance, sulphate is made containing only 0·007 per cent. of iron. Where, however, the purity of the sulphate is material, as for alkali-making, lead pans have been almost everywhere supplanted by cast-iron ones, first introduced in the year 1839, when J. C. Gamble took out a patent for them in lieu of the lead or brick pans, described on p. 38, whilst H. Lee, at Felling-on-Tyne, had at

the same time made the same invention. The lead pans are usually oblong, with a slanting side for pulling out the sulphate; the metal pans sometimes, but rarely, have the same shape; they are nearly always shallow dishes in the shape of a segment of a sphere, cast very thick; they will be described in detail further on.

The oldest sulphate-furnaces with open roasters were those constructed by Leblanc and known in France as *bastringues.* They are represented in figs. 19 & 20, and consist of the following parts.

Fig. 19.

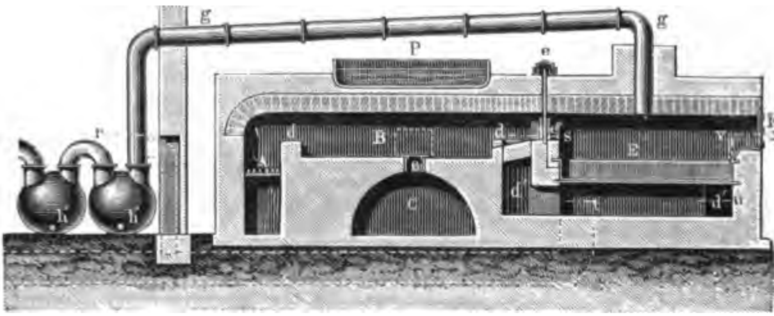
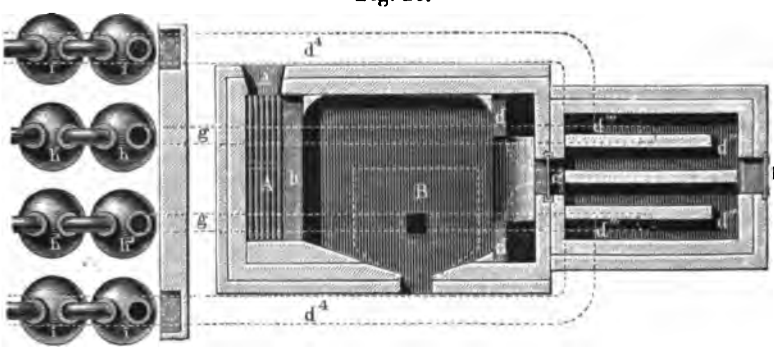


Fig. 20.



A fireplace, A, is heated by coals or, better, by coke; the flame travels over the bridge *b* into the furnace B, the bottom of which consists of very hard and closely placed fire-bricks on edge. Sometimes also siliceous stones are used for this, which do not wear away so quickly. This furnace, the *calcine,* serves for the second stage of the operation. A cast-iron damper, *e,* with a cast-on flange, whose turned-down edge dips into a gutter filled with sand, permits the opening or shutting off communication between the

gangway *e* of the calciner B and the pan-furnace or *cuvette* E. The bottom of the latter is made of hard sandstone or very thick lead, in the form of a shallow dish, resting upon a strong metal plate, or latterly altogether of cast iron, but always of rectangular shape and not very deep. It is covered by an arch pierced by one or two stoneware pipes, *g*, for carrying off the hydrochloric acid gas; the condensation of the latter in the Woulfe's bottles *h h* will be described in a subsequent chapter. The dish is heated from below by the fire-gas from A, which has already passed through B and charged itself there with acid vapours; they descend in two outlets, *d d*, at each side of the gangway *e'*, travel backwards and forwards below the pan in the flues *d'*, *d''*, and *d'''*, and then through the underground flues d^4 to the condensing-bottles *i i*, which communicate with a good chimney. Upon the top of the calciner B, or in some other suitable place, there is a lead pan P for heating the sulphuric acid serving for the decomposition of the salt.

The salt (according to Payen 250 kil. for each charge) is put in, as dry as possible, through the door K of the pan-furnace E, or preferably through a hopper provided with a damper set in the furnace-roof. There are often special contrivances for safely closing the door K. Figs. 21 & 22 represent one of these, in plan and in ele-

Fig. 21.

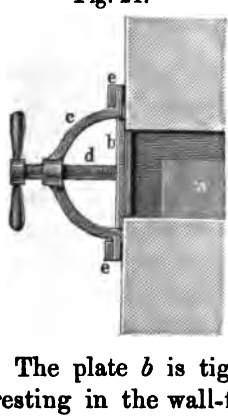


Fig. 22.

vation. The plate *b* is tightened by turning the screw *d* in the bow *c*, resting in the wall-fixed hooks *e e*. Then, by means of a bent funnel, the necessary sulphuric acid is run in from a measuring-vessel. According to Payen, for 250 kil. salt (theoretically requiring 269 kil. vitriol of 144° Tw.), 300 kil. (=167 litres) of vitriol are to be used, because towards the end of the operation sulphuric acid is volatilized. These proportions, if actually carried out, are very faulty.

Such an excess of vitriol is quite unnecessary, if the contents of E and B are carefully turned over; and it occasions a longer duration of the operation, together with much contamination of the hydrochloric acid. In Belgium, according to the official report of 1855, to 300 kil. salt 325 acid of 144° Tw. were taken; or 351 kil. salt for 380 to 390 acid, or 400 salt for 440 to 460 kil. acid, which is far too much. According to Kerl-Stohmann's 'Chemie' (v. p. 266), in 24 hours 4 charges are made, consisting of 250 kil. salt and 225 kil. vitriol of 144° Tw.; the latter agrees with the proportions employed at most large works, and seems to be correct, whilst the statements of Kopp and of the Belgian official report are either incorrect or prove very bad work.

Acid and salt are well mixed up together by means of iron rakes; then the door K is closed and luted. The reaction at once sets in, and is assisted by the indirect heat of the gas generated on calcining the preceding charge in the furnace B. Streams of almost pure hydrochloric acid escape, whose condensation in the two series of receivers h' is consequently very easy; often the mass swells so as to rise above the edge of the pan and up to the door. In England (where only cast-iron decomposing-pans are employed, no leaden ones) about ½ ounce of tallow or some cheaper grease is regularly put into the pan, to prevent boiling over; the grease is thrown in after the whole of the charge has been put in and well mixed up, just before the working-door is closed. The reaction gradually decreases; and when from two thirds up to three fourths of the gas has escaped, the mass assumes the consistency of a thick dough. Now the firing ceases for a time, the damper, *e*, is opened, and the half-finished mass is conveyed through e' into B, which in the meantime must have been emptied, by means of a large dished shovel. During this time it is difficult to avoid an escape of gas out of the working-door; a draught-hood over this is consequently advisable. Then the damper is lowered again, E is charged again with salt and acid, and the firing in A is at once recommenced. Now the decomposition is finished in B, by spreading the mass as evenly as possible on the hearth, where by the direct effect of the fire it soon passes from the dough-like condition into a dry, friable state. All the larger pieces are broken up and crushed down; and the mass is turned over thoroughly, so as to mix the bisulphate with the unattacked common salt and to induce a mutual reaction. The work is continued at a good red heat, hydrochloric acid escaping along

with a little sulphuric acid and being carried away by the fire-gas. The operation is considered finished when only one or two per cent. of free acid are left in the mass and it has become red-hot all over; then a plate, *c*, in the middle of the furnace is taken away, and the charge pulled down into the arched space C by means of a rake. This arch is accessible by a door from the front of the furnace; here the sulphate is cooled, and is only withdrawn just before finishing the next charge.

The duration of an operation varies a good deal. The stuff must not stop too long time in the pan, lest this should melt; but otherwise very good sulphate can be obtained, almost free from iron and containing very little undecomposed salt, and consequently well adapted for making white glass, window-glass, and even plate glass. According to Kopp (*vide* Wurtz, *l. c.*) a charge of 100 to 250 kil. of salt (2 to 5 cwt.) takes from 1½ to 3 hours; but according to the Belgian report (which in this respect is certainly trustworthy) the time is 6 to 8 hours in the pan, and 3 to 4 hours in the roaster; and this agrees with information personally collected from various sources by the author.

Kerl-Stohmann's 'Chemie' gives the following details as the most suitable dimensions of a furnace decomposing 250 kil. of salt with 225 kil. of vitriol of 144° Tw. every six hours:—

Length of the fire-grate (consisting of six grate-bars) 4 ft. 3½ in., width 1 ft. 9½ in.; firing-hole in front of the fireplace—length 3 ft. 6 in., width at the grate 1 ft. 11 in., at the outer furnace-wall 2 ft. 4 in.; fire-bridge same length as the grate, 8 in. wide, 7½ in. high; length of the roaster-bed 8 ft. 3 in., greatest width 7 ft. 6 in. to 8 ft. 3 in. The arch rests on a wall 12½ in. above the bed, and in its highest point rises to 1 ft. 9½ in. above the same. The flues *d d* are 1 ft. 3½ in. square. The wall separating the roaster from the pan-arch is 10½ in. thick; it projects 4 in. below the cast-iron plate, in order to support this. The arch of the roaster is dome-shaped, that of the pan barrel-shaped. The metal plates upon which the lead pan rests are 1¼ in. thick. The pan is 6 ft. 6½ in. long, 4 ft. 3 in. wide, 12½ in. high; the lead is 1¼ in. thick. The two stoneware pipes for carrying away the acid vapours are each 9¼ in. wide inside. The firing is done with coals, of which daily about 15 bushels are consumed.

This apparatus has undergone many modifications. Thus Kuhlmann (comp. Payen, p. 420) has the pan fixed just over the roaster,

so that the charge can be dropped directly into the latter. In other cases the pan, along with the tank for the sulphuric acid, is heated by a separate fire; and in this case less coke is used for the roaster; the latter is made correspondingly longer, in order to utilize the heat; and the gas is in this case not carried underneath the pan, which has its own fire, but straight into the condensing-apparatus.

In other cases the gas from the pan is allowed to mix with the fire-gas of the roaster, carrying the acid vapours from the same; then of course only one condensing-apparatus is provided, and strong acid cannot very well be made.

Often two pans are arranged for one roaster, because the work in these takes longer. Such a furnace is represented in figs. 23 to 26 on a scale of 1 to 50, according to the Belgian Report of 1855. Fig. 23 shows a sectional elevation on the line O P, and fig. 24 another on the line R S of the plan fig. 25; fig. 26 is a sectional elevation on the line T U. A is the roaster; B B′ are the pans; *a*, the fireplace. The doors *o o′*, opposite to each other, serve for charging the pans and pushing the mass into the roaster through *k k*, after pulling up the dampers *l l′*. E E are stoneware pipes for taking away the gas. The flame of the fireplace travels over the bed of the roaster, A, then, in two lateral flues underneath the pans, round the middle wall *e*, and through two other flues into the chimney, as shown by the arrows. Here also there are dampers, *f*, for regulating the draught. Near the door of the roaster (this is much better than in the centre, as shown in the drawing) there is an opening *n*, through which the finished mass is dropped into the cave C, where it cools. Each pan receives 300 kil. salt and 330 kil. acid of 144° Tw., which remain there 6 to 8 hours, so that the roaster, which only requires 3 to 4 hours, and is charged in turns from each of the two pans, does double the above-mentioned work. By means of the flues *d d′* and the dampers *m m′* the flame of the roaster can be directed at will over either of the pans, or over both at a time. The rule is, when one pan is being charged and the other one is half worked off, to direct the whole heat of the roaster to the latter; but when the charging is finished, the fire-damper leading to it is opened a little.

Lastly, at present, everywhere in Belgium is found the *muffle* or "blind roaster," mostly also with double lead pans. The furnace employed in 1855 at the Floreffe works has been described and figured in the Belgian Report, and from this has passed into several

Fig. 23.

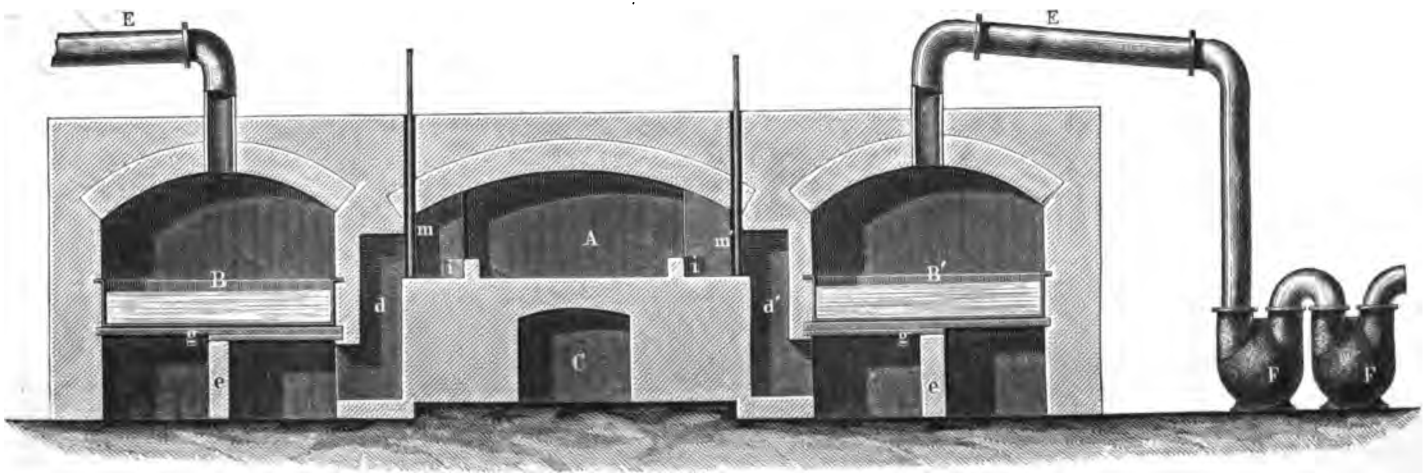


Fig. 24.

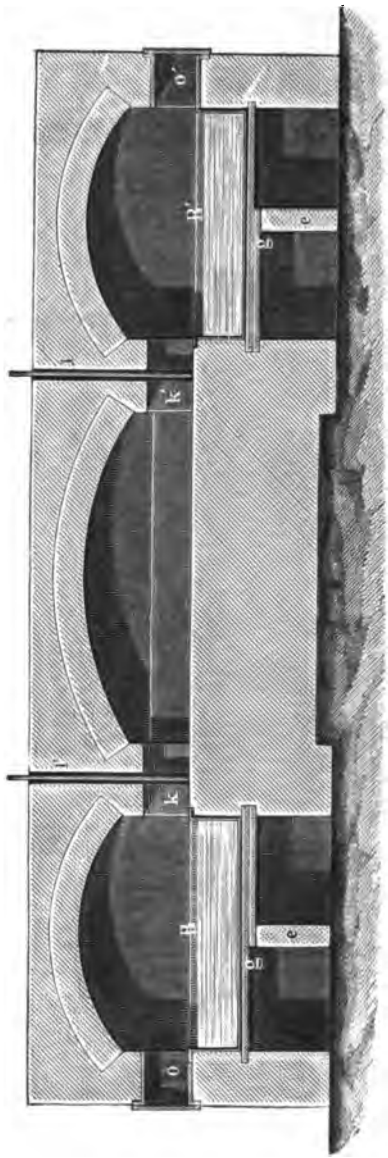


Fig. 25.

Scale $\frac{1}{50}$.

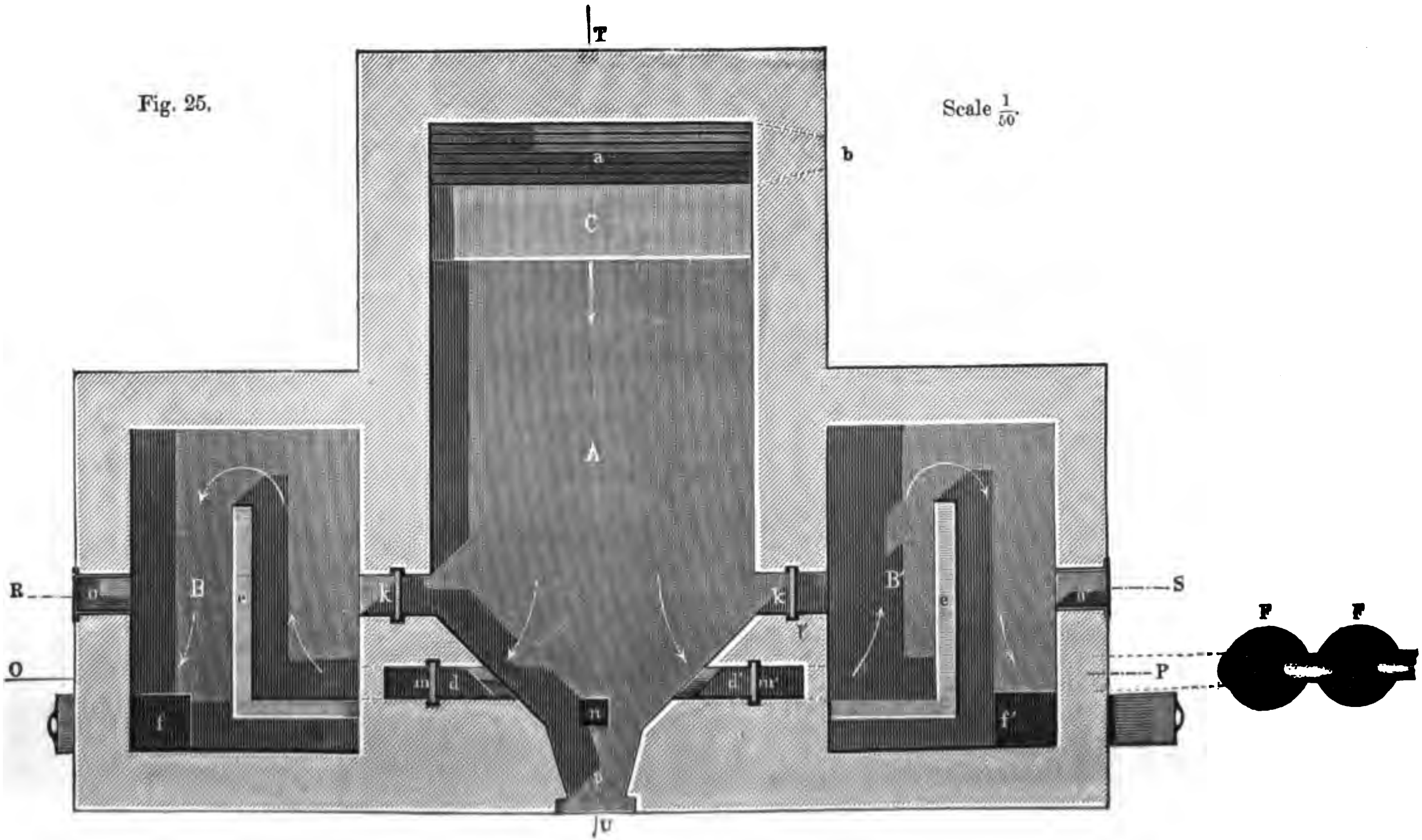
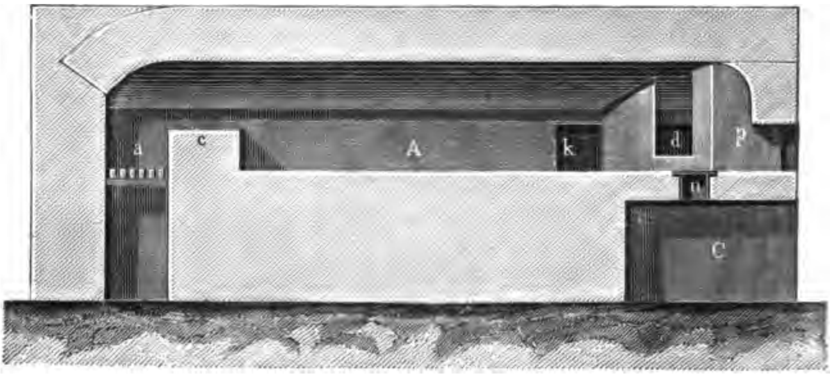


Fig. 26.



treatises. Instead of that, a more recent construction is actually at work in Belgium, here represented in one sectional elevation and two sectional plans (figs. 27 to 29). A is the fireplace, B the muffle; the flame passes between the muffle-arch *a* and the top arch *b*, which is made double, and contains an air-space *c* to lessen radiation. The air-channels *d d*, opening outside, serve for cooling and protecting the respective parts of the furnace. The flame descends in the flues *e e*, and passes through *ff* underneath the bottom, *g*, of the muffle; the latter is made specially strong near the fire end, on account of the danger of fluxing, and also at the back end. The openings *h h* serve for cleaning out the flues, and are usually closed. From the bottom of the muffle the fire either passes through *i* directly to the chimney, or first underneath the lead pans C C, the dampers *k k* permitting precise regulation. The plan fig. 28 shows very well how the pans are supported from below. The pans are ¾ in. thick, and stand on cast-iron plates, preferably double ones with 2 in. air-space between, to prevent the lead melting. Small holes can be repaired in the furnace itself; and one pan may be working while the other one is under repair. The air-channel *l* serves for cooling. The side of the pan next to the furnace slants upwards, so as to facilitate pushing the charge through the gangway, *m*, into the roaster, B. The damper *n* is usually shut, as the muffle-gas is strong enough to admit of being mixed with the pan-gas; but if muriatic acid free from sulphuric acid has to be made, the pan-gas must be separated from the roaster-gas by the damper *n*. The finished sulphate is drawn

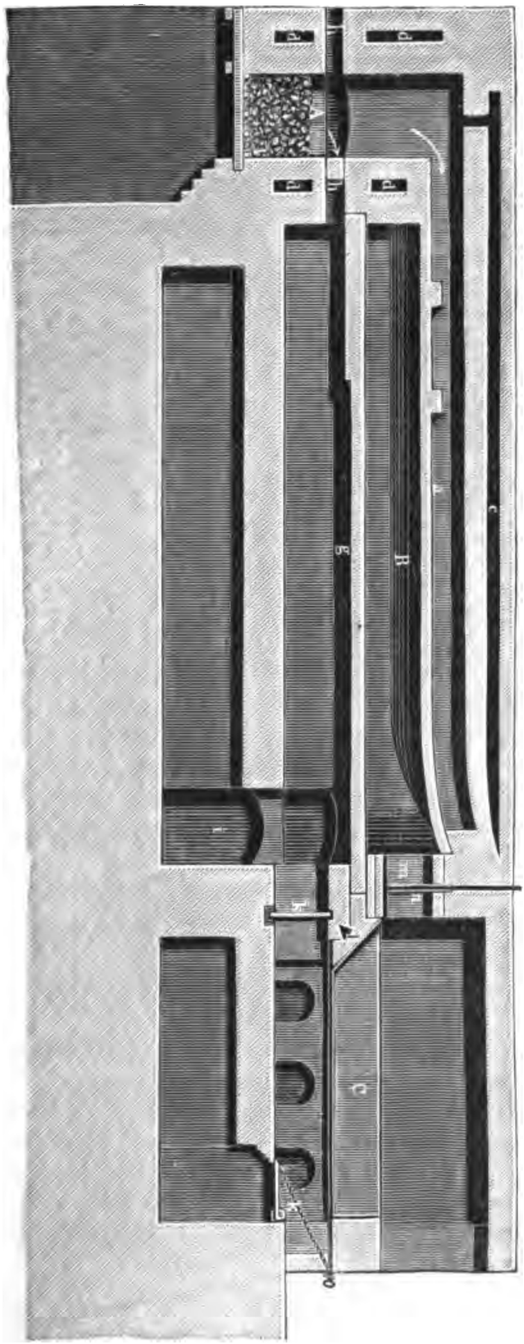


Fig. 27.

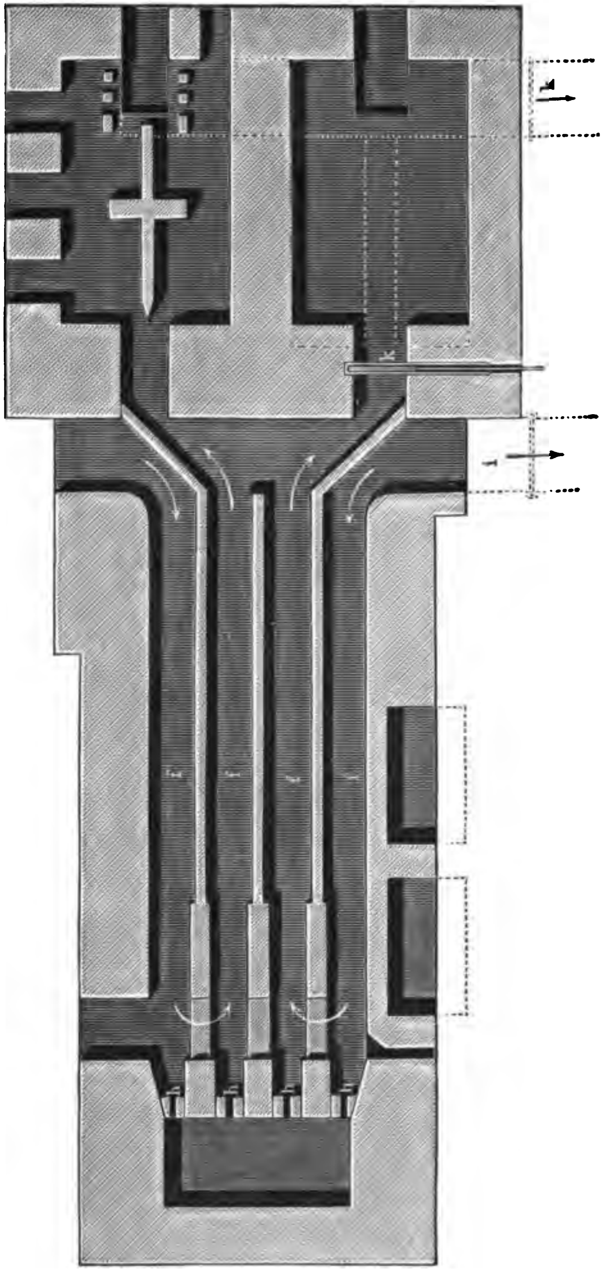


Fig. 28.

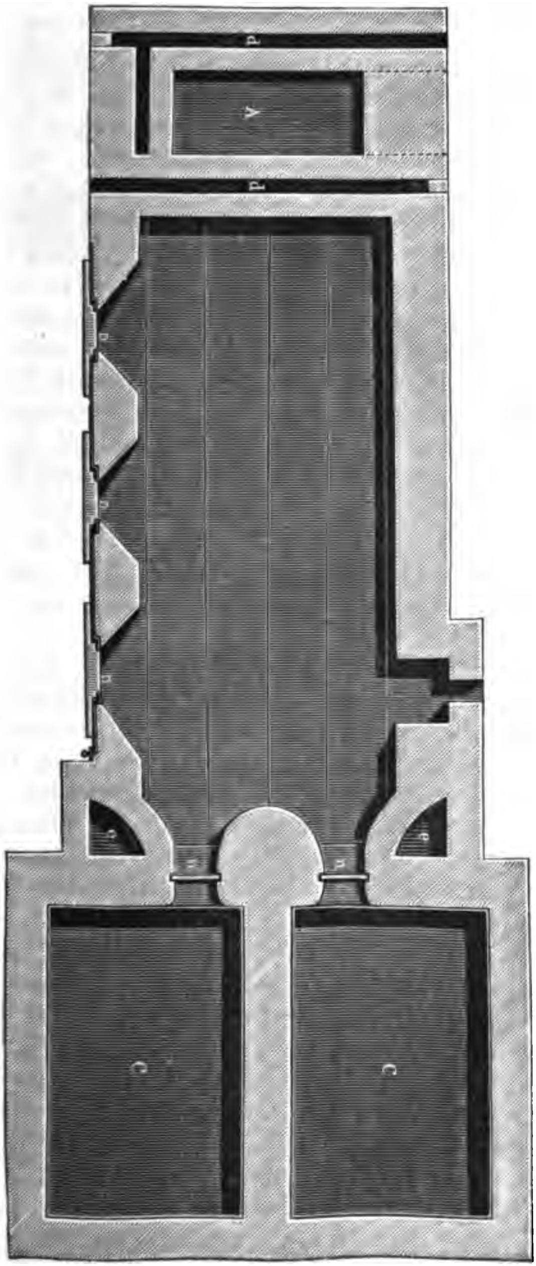


Fig. 20.

from the working-doors *o o* into boxes, in which it is wheeled away to the warehouses.

This furnace can put out as much as 5 tons of sulphate in 24 hours. Its exact dimensions are:—total length 39 ft.; outside width of the roaster 11 ft. 2 in., of the pan-furnaces 16 ft. 5 in.; grate 2 ft. 7½ in. wide, 5 ft. 11 in. long; height of the firebridge above the grates 5 ft. 11 in.; thickness of the side walls of the fireplace 2 ft., air-channels 4 in. wide; depth of the flue on the top of the muffle 12 in.; thickness of the upper arch 1 ft. 7½ in. (inclusive of a 5-in. air-course in the middle), of the muffle-arch 4 in., with a few strengthening ribs as shown in the diagram; thickness of the muffle-bottom 3 in., but in front and in the back 8 in.; inside length of the muffle 19 ft. 6 in., width 7 ft. 10½ in., up to the working-doors 9 ft. 2 in.; height up to the spring of the arch 8½ in., up to its crown 1 ft. 10 in.; gangway between the muffle and the pans 1 ft. 9 in. high, 1 ft. 4 in. wide; flue underneath the muffle 2 ft. 3½ in. in the middle; flues underneath the pans 1 ft. 7½ in. high; communication between the flue underneath the muffle and those underneath the pans 1 ft. 7½ in. square; pans ¾ in. thick, 7 ft. 10½ in. long at the bottom, 9 ft. 2 in. at the top, 5 ft. 11 in. wide, 1 ft. 5 in. deep.

The employment of a blind roaster is not at all indispensable for obtaining sulphate sufficiently pure for glass-making, especially with a deep fireplace as here designed and with moderate draught; it has been made compulsory in Belgium merely for the better condensation of the muriatic acid. We shall see below what rules have to be observed in this respect in the construction of blind roasters.

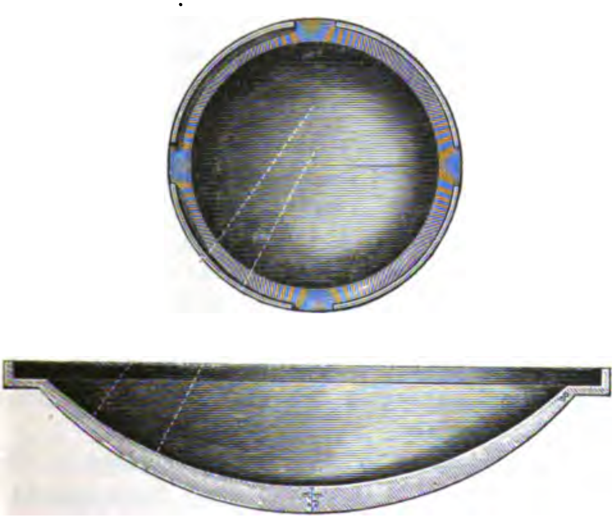
Much more widely used than the sulphate-furnaces with lead pans are those with *iron pans,* now employed wherever salt-cake is made for the manufacture of alkali. According to Henry Deacon (Chem. News, xxiii. p. 160), the first inventor of the present decomposing-pans was J. C. Gamble, who, on March 14, 1839, patented a kind of rectangular flat-bottomed retorts. Directly after, H. Lee, having opposed and defeated Gamble's patent, introduced a kind of pan, of the shape of a large cast-iron spoon, whose broader side was turned towards the workman, the smaller side towards the roaster. Now Gamble again followed with a round "pot," smaller and deeper than the present shape and placed in an outer pan for protection. From this the present shallow uncovered pan, directly exposed to the fire, has been developed.

In some rare cases the form of the pan resembles that of the lead pans just described; and they are then heated by the waste fire of the roaster, precisely in the same manner. Mostly, however,

Fig. 30.

Fig. 31.

Figs. 32 & 33.



they are shallow cast-iron dishes, 9 to 11 feet in diameter, and 1 foot 9 inches to 2 feet 6 inches deep; their thickness varies from

5 to 7 inches in the centre, and from 2 to 3 inches near the edge; their weight from 5 to 6½ tons. Their edge is either quite even (fig. 30), or provided with a plain horizontal flange (fig. 31) or with an upstanding margin on an horizontal flange (figs. 32 and 33). These forms differ especially in respect of the boiling-over of the mass and the escape of acid vapour. The cover is very frequently formed by an arch independent of the pan, so that the latter, if cracked, can be taken out without any loss of time and replaced by a new one; merely the front wall of the pan furnace above the fireplace need be taken away and rebuilt; and the exchange is all the easier, as the pans, from other practical motives, are always set so that their bottom is nearly on a level with the ground, and the fireplace is built underground: this is done in order to have the working-door of the pan just at the proper working height, say 2 feet to 2 feet 6 inches above the ground. In laying out the decomposing-house, care should be taken that sufficient free space remains in front of the pan-furnaces, so that the pan can be pulled out by means of a winch and a new pan can be run in, for which purpose, as no work is going on, all the furnacemen &c. will be disposable.

The pans usually have one or two lugs cast on, into which the chain of the winch is fastened. The new pan is placed on a strong wooden or iron bogie and run with this underneath the pan-arch, the bogie-wheels sliding on loose, flat, iron bars; the old pan is likewise run out on a bogie, or directly on the flat bars, previously greased with waggon-grease. At larger works there is always a pan ready on a bogie, or at least supported in such a way that a bogie can be run underneath and no time be lost; with energetic work no more than 12 to 15 hours need elapse between the beginning of pulling down the brickwork of the old pan and finishing that of the new pan. At some works, where all the pans are set in a single row, a railway runs parallel with them, which partly serves for taking away the salt-cake, partly also for taking out cracked pans and putting in new ones with the assistance of a travelling crane.

In the case just described the pan can be kept in use a good deal longer than usual, if turned 90° every three months, so that fresh surfaces are always offered to the wear and tear in the worst places; pans can thus be made to last for eighteen months.

It is not quite so convenient if the arch is not independent of

the pan, but rests upon the edge of the latter, as in fig. 33. Figs. 37 to 40 (pp. 74–77) show this arrangement. In other cases such pans are built with a straight cylindrical wall, resting on the pan-edge and covered by a horizontal circular metal plate. In this case, when the pan cracks, the top arch &c. must be taken down and rebuilt after putting in the new pan; this causes 12 to 16 hours' detention in addition to the time stated for resetting the pan with independent arch. The stoneware pipes for the acid gas, starting from the centre of the pan-arch, must be carried in the timber of the roof in such a way that they need not be taken away when the arch is pulled down; there is no question of this where the pipes are placed sideways.

The reason why such an arrangement has recently been preferred at many works, although the pan-arch has to be rebuilt every time, and thus time and wages are lost, is that only in this way can an escape of acid vapours into the chimney be with certainty prevented. With the ordinary pans (fig. 30 or 31) standing loosely within an arch and either just touching it with their edges or connected with it by a low wall, it is very likely to happen that, on the contents of the pan boiling over (which cannot always be prevented), the acid will partly destroy the brickwork and open a slight communication between the space above the pan and that below it (viz. the fireplace). By the expansion and contraction resulting from great changes of temperature the pan is already loosened and is easily detached from the arch, so that cracks and other communications of the kind just mentioned are formed. But since the draught of the chimney serving the fireplace is necessarily much stronger than that of the condensing-apparatus, which is in connexion with the space above the pan, a good deal of the gas given off from the pan will inevitably be drawn downwards into the fireplace and thus escape directly into the chimney, as soon as the least communication exists between the space above and that below the pan. The smallest hole suffices for this; and it may last a long time, and much nuisance and damage may have been caused by the escape of muriatic gas before it is even noticed. This drawback is thoroughly prevented by the arrangement of resting the arch on the pan-edge itself, if the latter is bent upwards and visible outside, as shown in figs. 37 and 40; for even if a hole is made in the pan by any acid boiling over, which cannot happen so easily on account of the

turned-up flange, the gas issuing from it must escape into the working-space itself and must be noticed directly; in no case can it get into the fireplace.

An arrangement figured in Muspratt's 'Chemistry' (iii. p. 908), thence copied into many text-books, and also greatly recommended in Hofmann's 'Report by the Juries' (1862), seems to be obsolete now in England, but has been found by the author in a German works. It consists in providing the pans with sheet-iron dome-shaped covers, bricked over; the flame of the fireplace first travels over these covers, and then underneath the pan-bottom. The whole is a closed iron muffle, only provided with openings for charging, shoving, and carrying off the gas. This construction is costly and complicated; it makes the renewal of a pan more troublesome, and facilitates the escape of acid vapours by any hole in the iron dome; the heating from above does no good, except indirectly by keeping the direct flame off the pan-bottom, which can be easily done in any case by proper setting, as we shall see below. In fact, at the German works where this style of cover has been adopted, the fire first goes underneath the pan-bottom and then over the top, where its only use is to protect the dome from being acted upon by the acid vapour, by keeping it hot. The arrangement drawn by Muspratt has never been general in Lancashire, as erroneously reported by Hofmann; it was only adopted at a few works, and seems to have been given up everywhere for years past. Another arrangement (not to be confounded with this, and still found at some Lancashire works) consists of cast-iron domes for the pans, without any fire passing over them; they stand in the place of pan-arches; and on the occasion of renewing a pan its dome can be pulled up and let down again. Sometimes they are covered with bricks to keep them hot, and thus protect them from the acid vapours.

The *material* of the pan is of the last importance for its durability. It should be considered what demands are made on such a casting. It is expected to stand the change of temperature between the cold salt and the acid, heated at most to 100° C., on the one hand, and the low red heat required by the reaction on the other hand, and constantly back again, without cracking, and must even stand, to a certain extent, the caking-on of crusts and the great local superheating consequent upon this, notwithstanding the great thickness which is given to it for the sake of durability.

It is further to resist the attack of the fire from below and the much worse attack of the hot acids and the fusing bisulphate from above. In fact, even under the most favourable conditions, it can do this only for a certain time; a pan is considered to have done good service indeed if it works nine months and furnishes 2500 tons of sulphate. Sometimes they last longer—up to 4000 tons, but mostly much less; and now and then they crack after a few days' use. In order to stand at all, they must consist of a mixture of several brands of pig iron (kept secret by the founders), and must be cast with the greatest care. Pure charcoal pig, for instance, resists cracking by changes of temperature better than coke pig, but it is too soft and too easily attacked by acids. The pans are of course cast in loam—not in bricked-out pits, however, but in cast-iron moulds thickly lined with loam, placed bottom upwards, and provided with many holes for the escape of gas; a feeding-head of 9 inches diameter and 2 feet height produces a dense casting, every blister, of course, making the pan useless. In England the casting of decomposing-pans was formerly a monopoly of Messrs. R. Daglish and Co., of St. Helens, and the Widnes Foundry Company, of Widnes; for a number of years past several other foundries have also successfully taken up this article, as Messrs. John Abbot and Co., of Gateshead, William Black, of South Shields, &c. On the Continent, the decomposing-pans must generally be taken from the nearest foundry at which they can be obtained; the alkali-works are therefore nearly always compelled to abstain from heating them directly, and to employ merely the waste heat of the roaster; so that their whole style of working is different. There the pans rarely last, on an average, above 1500 tons of sulphate. They will last the longer if the mixture is conveyed from them into the calcining-furnace in a thinner state.

It is hardly necessary to mention that the way of *setting the pans* (which will be described in detail lower down), and especially also the *treatment* of the pans, have very much to do with their durability, and that only very reliable and skilled men should be employed upon them. If the workman allows thick crusts to cake to his pan and, perhaps, pushes them off again suddenly, if he allows the pan to become red hot towards the finish of the operation, and then at once charges it again with cold salt and acid, and so forth, the best pan may be cracked. This is at once perceived

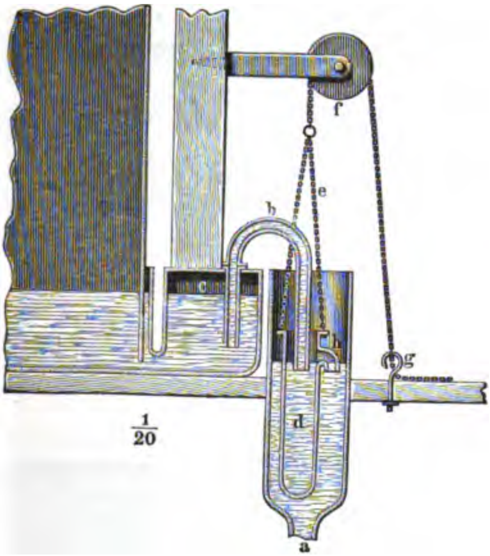
through melted bisulphate getting into the fireplace; and in this case it is the rule in the best works to stop the works *at once* and to replace the cracked pan by a new one. It is often possible to work on a few days with a cracked pan, but with great loss of sulphate and gas: nor is it practically possible to patch it; for riveting, cementing, &c. do no good, as has been proved by innumerable attempts.

The lower portions of the pan-setting, such as the fireplace itself, the arch over the same, the annular wall carrying the pan-edge, &c., are touched as little as possible on resetting a pan, unless they require repairing at the same time. The *fireplace* must, in any case, be constructed so as to avoid overheating single parts of the pan-bottom, by which it would be most readily cracked: that this happens through unequal heating of single places can be perceived on cleaning out the pan, the respective places appearing more brightly red-hot than the remainder. Frequently this can be remedied by enlarging or narrowing one or more of the "snore-holes" an inch or two; and the practised eye of a skilled furnace-builder must here frequently supplement the drawings. In order to avoid the damaging action of the direct flame, the firegrate is either placed very much below the pan, or a perforated (pigeon-holed) arch is placed between, as the diagrams will show.

At some alkali-works the sulphuric acid, which is conveyed direct from the sulphuric-acid works in a lead tube, arrives sufficiently hot, for instance from the Glover-tower or from a tank where tower-acid and chamber-acid are mixed. But where this is not the case, there ought always to be a special small pan provided for *heating the sulphuric acid,* made of cast-iron lined with lead, heated by the waste heat of the pan-fire and at the same time serving for measuring off the acid required for each operation. It is for this purpose furnished with a glass float or with a fixed leaden scale. The outflow of the acid from the measuring-box into the pan is produced by a perpetually filled siphon, for instance one like fig. 34. The sulphuric acid here is heated up to 80° or 100° C.; without this it is much more difficult to keep the decomposing-pan from cracking.

The *running-in of the acid* into the pan has also to be carefully attended to. If there is sufficient fall at disposal, the acid ought always to be run in at the top, in the centre of the pan-arch or close to it; for this purpose there is usually a short cast-iron

Fig. 34.



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pipe provided, firmly connected on the outside with the lead pipe conveying the acid from the measuring-box, and frequently ending inside with a rose for scattering the acid in a fine spray. In this case the acid always runs onto the salt previously thrown in, without coming into immediate contact with the pan, and the cast-iron pipe itself lasts pretty long, because it becomes hot and no acid can ever lodge in it. If, however, the measuring-vessel has to be placed lower down and the acid must be run into the pan sideways, this must never be done along the edge of the pan, because thus a channel will soon be formed in this place, and a crack will be the consequence. In that case the lead pipe must be put into a cast-iron one, projecting pretty far into the pan, so that the acid may get to the salt itself without running down the pan. This pipe will not last long; but it can be used somewhat longer by being turned. Stoneware pipes &c. cannot be employed, even if they would stand the changes of temperature, because the men too often push against them with their tools.

Figs 35 & 36 show a *salt-cake furnace with one pan and two open roasters*, at the works of Messrs. J. Hutchinson and Co., of Widnes.

Fig. 35.

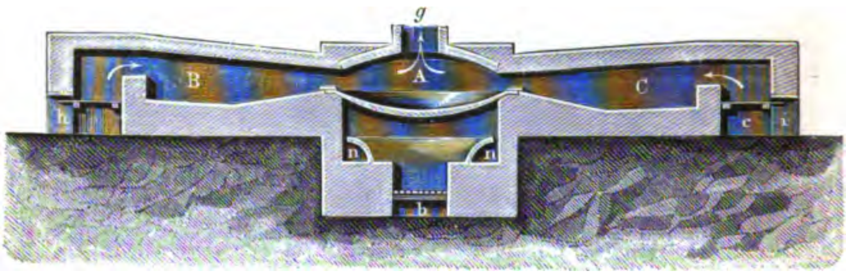
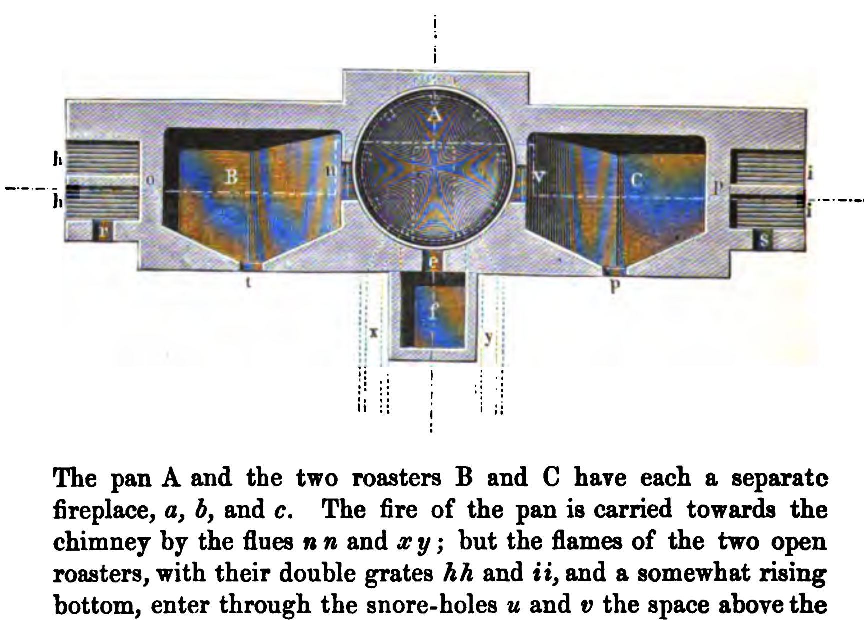


Fig. 36.



The pan A and the two roasters B and C have each a separate fireplace, *a, b,* and *c.* The fire of the pan is carried towards the chimney by the flues *n n* and *x y*; but the flames of the two open roasters, with their double grates *hh* and *ii*, and a somewhat rising bottom, enter through the snore-holes *u* and *v* the space above the pan. After having in B and C received the gas of the charges that are getting finished, they receive in A the stronger pan-gas, and ultimately pass through the fireclay pipe *g* to the condensers. *r* and *s* are the fire-doors of the roasters; *f* the firing-cave, *e* the fire-door, of the pan; *t* and *p* the working-doors of the roasters. By the fact of the roaster-fire touching the pan from above, the latter works so fast that it can supply two roasters. This arrangement is good for putting out a large quantity of salt-cake; but, owing

to the acid vapours all being mixed with fire-gas, only muriatic acid of 4° to 6° Tw. can be condensed, which is partly used for bicarbonate, but mostly run to waste. Pans with the roaster-fire heating them from the top are therefore only exceptionally met with. Now that muriatic acid forms an essential economical factor at alkali-works, such an arrangement appears very irrational.

Much better is the combination where the pan-gas and the roaster-gas are taken away separately. Such a construction, which has in practice proved entirely successful, is represented in figs. 37 to 40.

The diagrams will be understood without much explanation; and all the dimensions are marked (in metrical measure). Fig. 37 is a sectional elevation through the line A B of the plan; fig. 38 a sectional plan through the line C D of the preceding figure; fig. 39 an outside elevation; fig. 40 a sectional elevation through the line E F of the plan. The pan is in this case provided with a flange and upturned edge and a dome-shaped roof, which, to be sure, has to be taken down and built up every time a new pan has to be put in; but this only takes a few hours, and the arrangement affords absolute security against any escape of muriatic acid gas from the pan into the chimney.

The fire of the roaster travels from the grate *a*, through the roaster *b*, into the flue *c*, and then into the condenser for roaster-acid; the gas of the pan *d* goes independently through *e* into the pan-condensers. The roaster has two working-holes *ff*, with bars for supporting the tools, and with doors made of a fireclay tile in an iron frame, balanced by a chain, pulley, and weight, as shown at *g*. *h* is a balanced double damper of cast-iron, running in a groove of the gangway between pan and roaster, and luted with salt. Such double dampers, kept asunder by stay-bolts, are preferred, because single dampers are very quickly worn out at the edges by the acid vapours, and then allow the pan-gas from *d* partly to escape into the better-drawing calciner *b*; since the space between the two damper-plates is equally filled with salt, it is kept sufficiently gas-tight. The flange of the pan is interrupted at *i* and *k* for the charging-door and the shoving-hole. *l* is the funnel for the sulphuric acid, which, if there is a fall, is better placed near the centre of the arch, so that the acid will run into the middle of the pan onto the salt; otherwise, as mentioned above, a cast-iron pipe (quickly

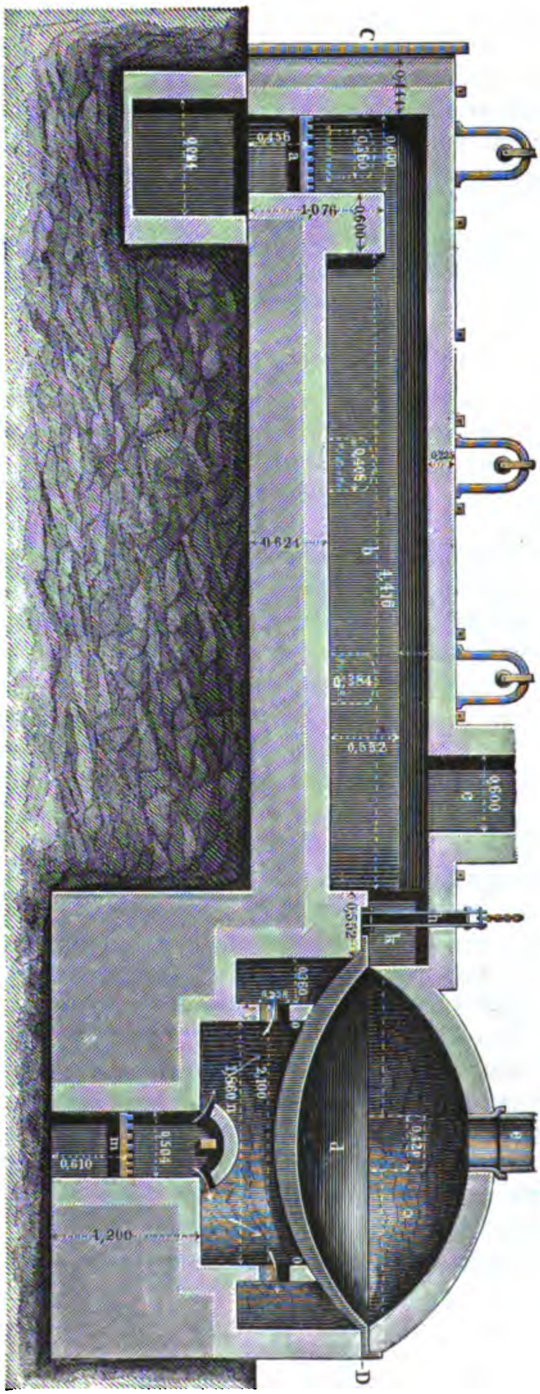


Fig. 37.

Fig. 38.

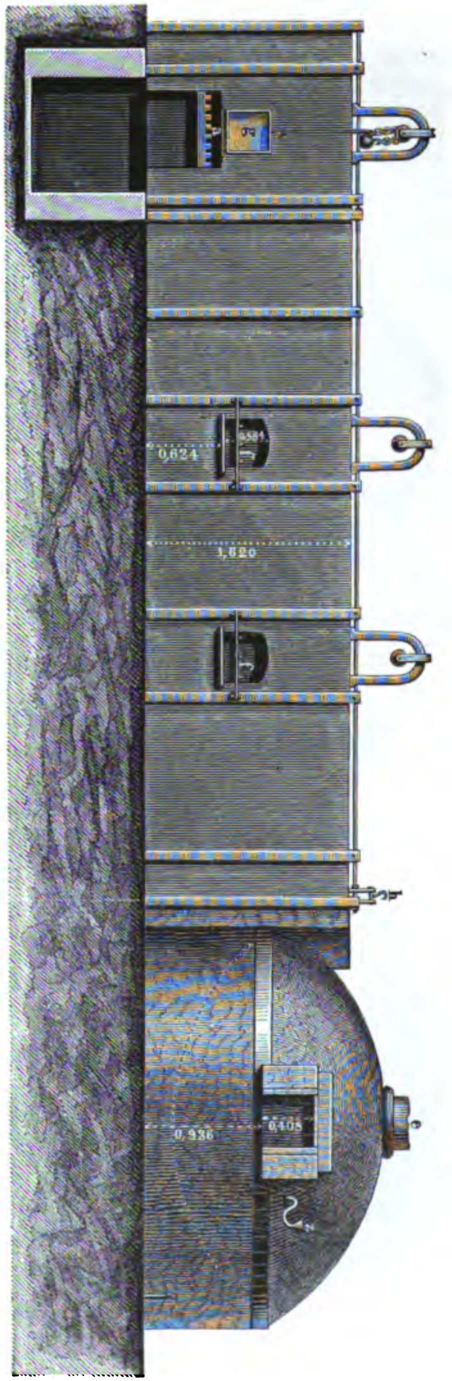
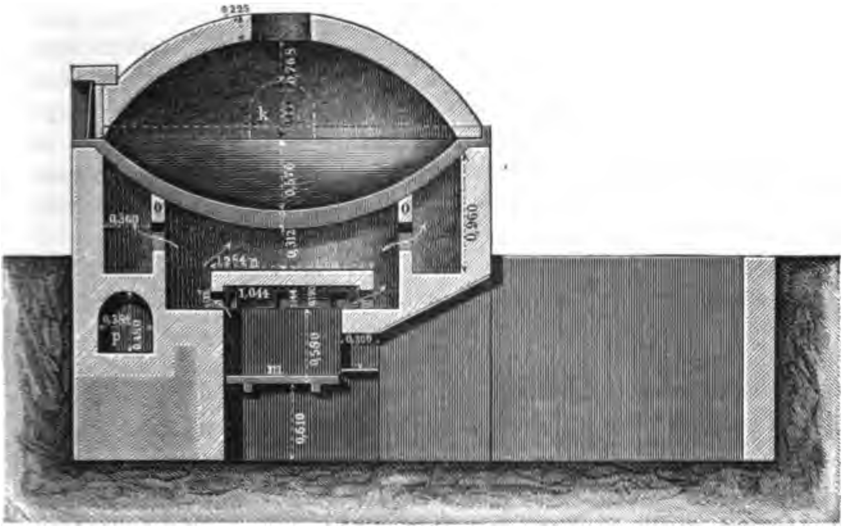


Fig. 39.

Fig. 40.



wearing out) has to be used. The diagrams show how the fireplace below the pan is laid out so as to protect the pan-bottom from the direct action of the fire, and to heat it as equally as possible; the sizes of the snore-holes &c. are all results of experience. Exactly the same sizes must be chosen if the pan is not, as drawn here, provided with a dome resting upon its own flange, but with a barrel-arch independent of it. The fire on the grate *m* is covered by the arch *n*, which is pierced only sideways with holes, whose section becomes larger from front to back; thus the pan-bottom is not in direct contact with the fire. The fire travels round the pan; but it is first kept in by the circular wall *o o*, and escapes only by its holes, different in size, according to the direction of the draught, into the outer annular space, where it heats the upper part of the pan, and ultimately into the flue *p*.

In the case represented here the pan is placed at the end of the roaster, and both are charged at the same side. Consequently the working-door of the pan is at right angles with the shoving-hole. The conveyance of the half-finished sulphate is effected by "casting" it with a long-handled shovel, curved so as to fit the pan-bottom. Such pans are called "casting-pans." If the shoving-hole is just opposite the working-door, the charge is pushed or

shoved over with a long-handled rake shaped so as to fit the pan-bottom; and the pan is called a "shoving-pan." The former kind of labour is rather easier than the latter; but the arrangements must suit the locality. Sometimes placing the pan in the centre of the back of the roaster cannot be avoided; in that case the charge must always be "shoved." The fireplace of the pan may also be placed sideways, instead of endways, but preferably not at the same side as the working-door, because then the firing-cave would have to be arched over.

The open roasters are heated either by coke or coals. The former is much dearer than the latter, especially as the cheaper gas-cokes do not answer very well, since they burn away quickly; and in the end the more expensive oven-cokes pay better, because there is much less of them used. Many works burn their own coke for this purpose from suitable coals. Still coke fires are mostly preferred to coal, because with the latter very much soot is formed, the fire-gas being considerably cooled by the evolution of acid vapours on the roaster-bed; and that the pipes and condensers may not get stopped up with soot, the former must be made very wide, and the latter packed very openly with loosely-placed bricks. They must also be fed with a strong jet of water, in order to wash the soot off the bricks; so that it is not very well possible to obtain strong acid. The condensed acid, mostly only 4° to 6° Tw., containing very much soot, will only do for evolving carbonic acid for the manufacture of bicarbonate, hardly even for the recovery of sulphur from alkali-waste. On the other hand, if coke is used in the roasters, the condensers can be packed much more closely, as no soot has to be dealt with; the water need not be run in a strong jet, and acid of 23° to 28° Tw. can be obtained which will do very well for making chlorine, and which, by suitable means, can be made even stronger, as we shall see below.

The *blind roasters* (muffle furnaces), for calcining the half-finished sulphate, are distinguished from the just-described open roasters by the fact that the flame in them does not come into immediate contact with the charge, but only acts indirectly through the bed and the arched roof, which together form a closed muffle. Accordingly the acid vapour formed in calcining is not mixed with fire-gas, and can thus be condensed much more easily than the gas from open roasters, as it is both less dilute and not so hot. It is not, to be sure, so strong as the pan-gas, as it is mixed with more

air, which gets in through the working-doors during the turning-over of the charge; it is also much hotter and less pure than pan-gas, owing to the sulphuric acid escaping during the finishing operation.

At many works, accordingly, the gas from blind roasters is condensed separately from the pan-gas, especially if acid is made for sale; where all the acid is used up at the works, the gases mostly go into the same condenser. One instance of a blind roaster has already been given in connexion with a lead pan. Another construction is shown in figs. 41 to 47, where the pan and the roaster have a separate fire each, which is necessary in forced work, such as is usual in England.

Fig. 41.

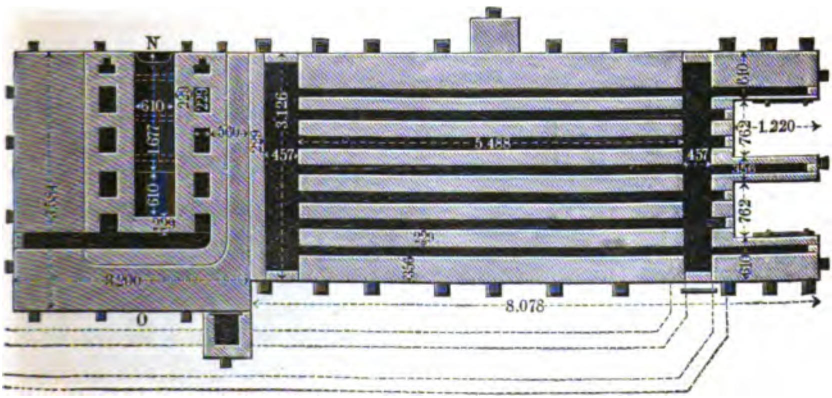


Fig. 42.

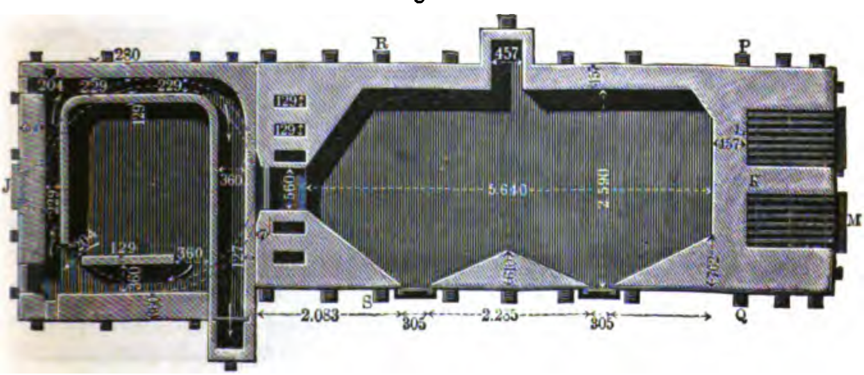


Fig. 43.

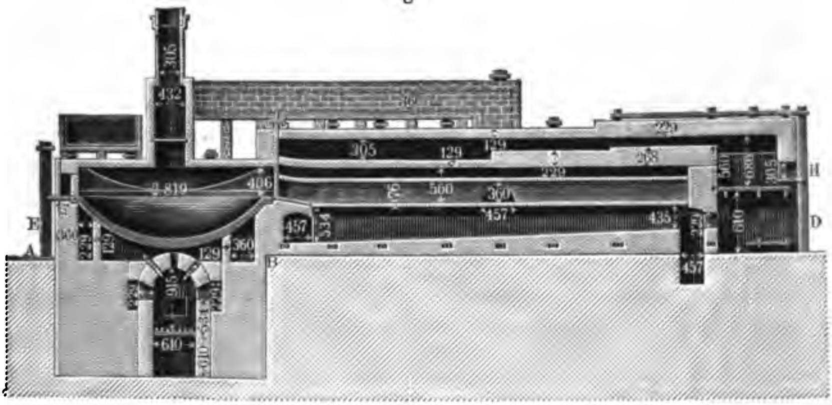


Fig. 44.

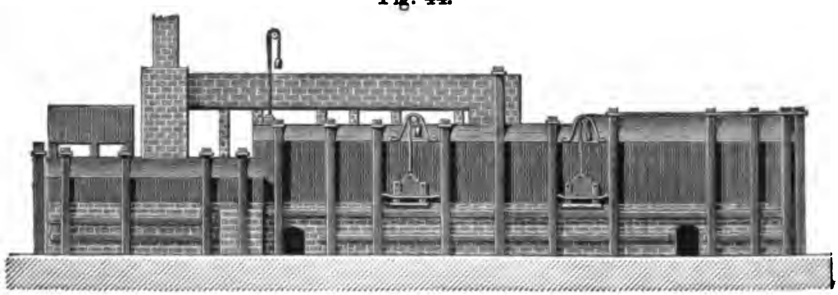


Fig. 45.

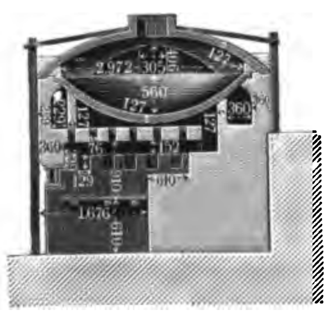


Fig. 46.

Fig. 47.

The muffle-arch behind the firebridge, where the first heat of the fire meets it, is a full brick strong, and covered besides with "half-thicks;" these are left out in the second third of the length; and the last third is only half a brick strong. The whole arch is covered with an inch of fireclay, moistened with weak soda-liquor; by this it is caused to frit together and to become more gas-tight. Of course the best fire-bricks must be employed, the joints must be made very narrow, and the whole masonry must be as solid as possible. The best height for the arch is 9 inches: less cannot well be taken without detracting from its stability; and if it is made higher, the radiant heat acts less upon the charge. It springs at a height of 12 inches from the bed, so that its crown is 21 inches above the same. The upper arch at the widest place is 12 inches apart from the muffle-arch; at the narrowest (in front) it is only 6 inches. Both arches are supported on metal plates covering the furnace from the outside, and held together by uprights and bracing-rods. In front the plates are 3 feet high, at the back only 2 feet. They are about 1 inch thick, and on each long side require 10 uprights, usually formed of 4-inch railway rails, and cross bars of $\frac{3}{4}$-inch square or $\frac{7}{8}$-inch round iron. The flames of the two fire-places travel over the muffle-arch divided by a thin wall, and unite at the far end, and then descend by several down-draughts. Here is also the gangway between pan and roaster, together with its damper.

These parts of the furnace must be very carefully built, as they are very much exposed to wear and tear.

The gangway is all lined with metal plates. The damper has a projecting top flange for a sand lute. It wears out very quickly; and a double damper, as in fig. 37, is preferable here also. Below the gangway the flues unite into a common cross flue; and the

flame again travels towards the front in seven narrow flues; it is here reunited by another cross flue, and at last carried towards the chimney. The seven narrow flues are so made in order to allow the furnace-bed to be made of ordinary 9-inch fire-bricks, which are employed on the flat, or 2½ inches thick. It is preferable to employ two courses of half-thicks (split bricks), crossing each other. The dwarf walls separating the flues should be 9 inches thick, so as not to burn away too quickly. The flues are 5 inches wide; so that a 9-inch brick has a good hold on each side; and in the front they are continued into cleaning-out holes, usually closed. The bottom of these flues is strongly inclined towards one of the cross flues (fig. 43), to facilitate cleaning. The acid gas is taken away by a lateral ascending channel, sometimes by a cast-iron pipe lined with bricks, passing through both arches; but the latter quickly wears out, and may cause the muffle-arch to crack.

Instead of making the furnace-bed of 9-in. fire-bricks, at many works fireclay slabs up to 2 feet square are employed; then the number of bottom flues is diminished to four. An instance of this kind is the furnace represented in figs. 48 to 50. The flame, travelling from front to back over the arch, returns in two lateral flues underneath the bed and again goes forward in two other central flues. In the furnace sketched in figs. 51 to 54 the course of the fire can be followed without any further explanation. If very good fireclay slabs can be had, the construction shown in figs. 48 to 50 is preferable to that shown in figs. 41 to 47, since

Fig. 48.

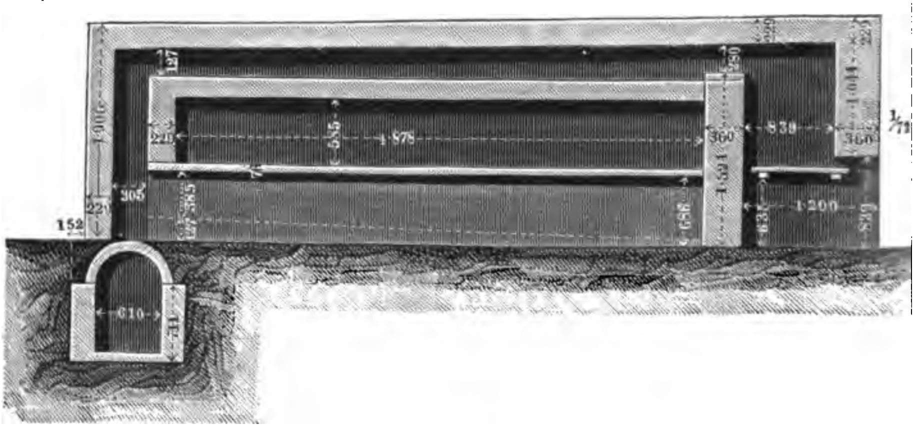


Fig. 49.

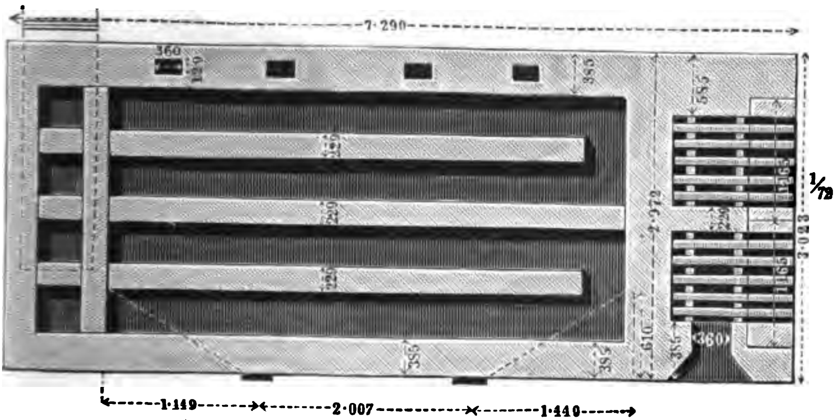


Fig. 50.

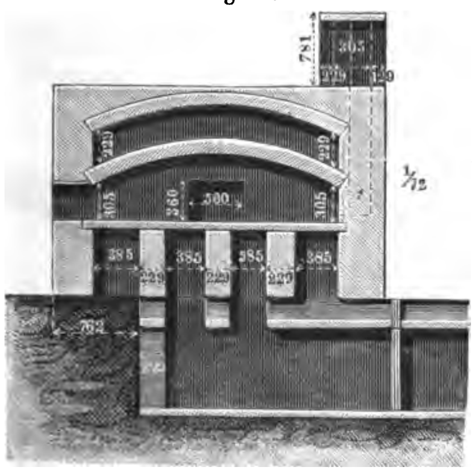


Fig. 51.

Fig. 52.

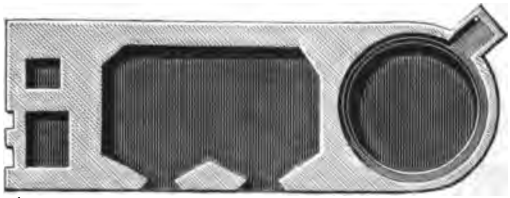


Fig. 53.

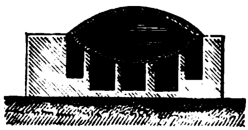
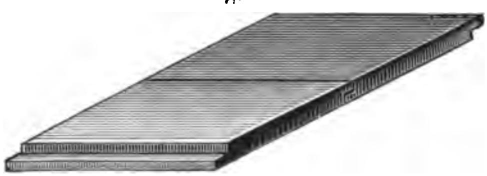


Fig. 54.

the bottom flues are more easily cleaned out; there are also much fewer joints in the bed. The fireclay slabs must, however, be of very good quality for this, and must be made with rabbited ends, as shown in fig. 55.

Fig. 55.



The muffles are frequently made much longer than they are drawn here—for instance, 25 or even 30 feet long inside; they cannot be made any wider, owing to the difficulty that would occasion in turning over the charge. By making the muffle as large as possible, both the heat of the fuel is better utilized, and the layer of stuff is much thinner, and therefore much more easily turned over and mixed.

We shall lastly give the description of a salt-cake furnace without a separate fire for the pan, as used in Germany, from Knapp's Chem. Technologie, ii. p. 391.

Fig. 56 is a sectional elevation, fig. 57 another at right angles through the muffle, fig. 58 a sectional plan on the level of the

Fig. 56.

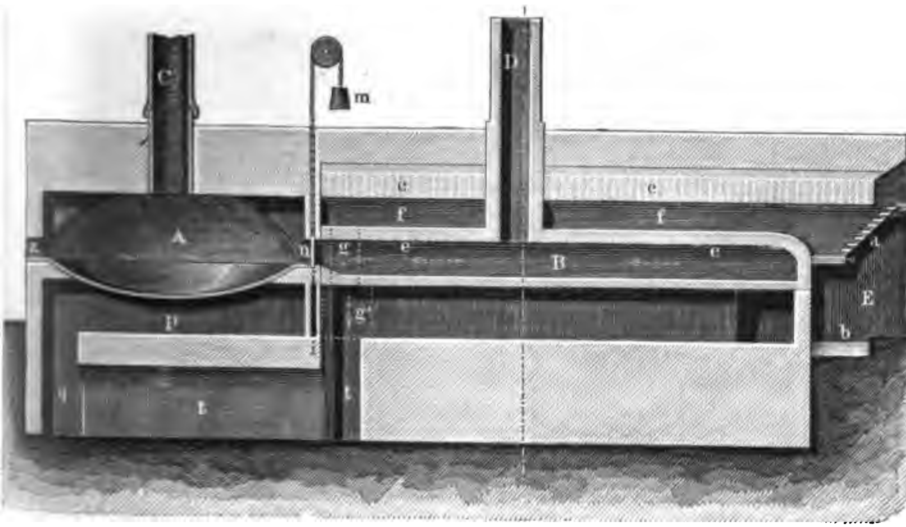


Fig. 57.

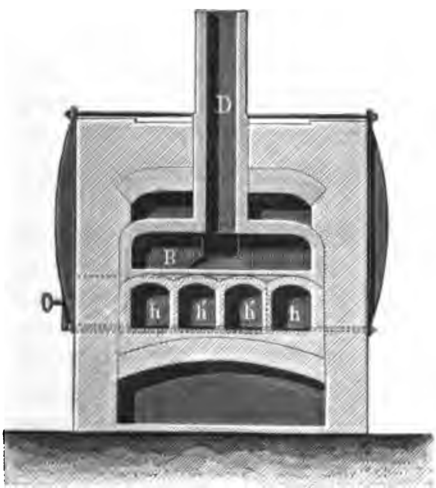


Fig. 58.

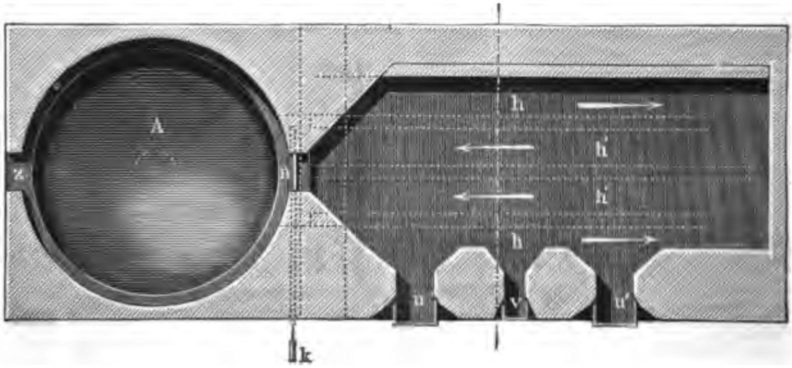
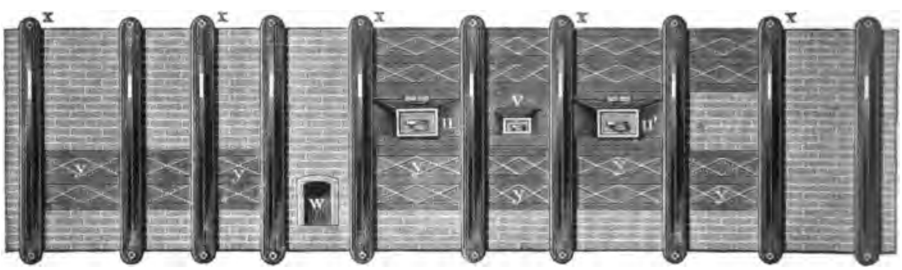


Fig. 59.



working-doors, fig. 59 a side elevation. The pan A, arched over with firebricks, and the roaster B are heated by the same fire, which first touches the latter, then the pan. The fireplace E is provided with a ladder grate *a* for brown coals; the ash-pan *b* is filled with water. The flame first travels over the muffle through *f*, between the roaster-arch *e* and the upper arch *c*, and then descends through the snore-holes *g* and *g'* (shown by dotted lines), in order to travel underneath the furnace-bottom, first through the two outer flues *h h* and back again through the two inner flues *h' h'* towards the pan. According to the position of the damper *i i* (regulated at *k*), the flame can either be directed underneath the pan, at *p*, and into the flue *q* leading to the chimney, or, when the damper is closed, immediately through *t* into *q*. The acid gas is carried away to the condensers separately from the pan by the stoneware pipe C, and from the roaster by the flue D. The salt is

charged through *z*, and the sulphuric acid through a lead pipe fixed in the pan-arch. The gangway *n* can be closed by a damper provided with the balance-weight *m*; *u*, *u'*, and *v* are the three working-doors of the roaster. *w* is a door for cleaning out the flue *t*; *x* and *y*, the iron bindings of the furnace.

The English blind roasters have usually a separate fireplace for the pan, whilst in Belgium, Germany, and France the pan is mostly heated by the waste heat of the roaster. This plan is not at all economical where a very large quantity of work has to be got out; for whatever is saved in coals is more than outweighed by the increased labour, the multiplication of furnaces, &c. In the Belgian works, according to Chandelon (Monit. Scient. 1864, p. 50), a blind roaster decomposes about 30 to 36 cwt. of salt in 24 hours; in Lancashire, however, he states the daily make at 11 to 12 tons of salt. The latter is exaggerated; 5 tons of salt daily is a fair average, 8 tons a very good make for a blind roaster; 12 tons daily are only decomposed in open roasters, and even with these but rarely, 10 tons being considered very fair work. In France and Germany, even in large blind roasters, the usual quantity of salt decomposed is 2½ tons in 24 hours, rarely 3 tons; according to Chandelon's latest report (Bull. Soc. Enc. 1871, xviii. p. 322) most Belgian works decompose not more than 36 cwt., and very few as much as 72 cwt. With this slow work, certainly, the muriatic acid can be more completely condensed than with very quick work.

A peculiar construction is that sketched in the 6th Report by the Inspector on the Alkali Act, p. 66. In order to avoid the drawback of a complicated construction, and the liability to getting out of repair, of the blind roasters, only the bottom of the roaster is fired, and that from below, thus doing away with the risk arising from cracks in the arch. The heat is very equally divided by flues; so that the bottom does not burn through very quickly. The flame afterwards heats the pan; and altogether the coal used is said to amount to 33 per cent. of the weight of salt decomposed. The pan-gas goes away along with the roaster-gas, which is not mixed with fire-gas. This style of furnace has not been adopted elsewhere.

Whether for calcining the half-finished salt-cake *blind* or *open roasters* are preferable, is still an open question. In the Tyne district none but open roasters are found; but in Lancashire these are employed only where no strong muriatic acid is made, other-

wise blind roasters alone are used. Messrs. Tennant have got blind roasters at the older works near Glasgow, but open ones at the new works at Hebburn. This alone proves that something is to be said on both sides. The advantages of *blind roasters* are as follows :—

1st. Better condensation of the hydrochloric acid.

2nd. Stronger muriatic acid.

3rd. Cheaper condensing-plant.

4th. The employment of coals for firing.

5th. A saving of sulphuric acid.

The advantages of *open roasters* are :—

1st. A larger turn-out of sulphate.

2nd. Less liability to need repairs.

3rd. The impossibility of acid vapours escaping otherwise than into the condenser.

4th. Greater facility of making strong sulphate.

Of course the circumstances that appear as advantages of blind roasters, correspond to drawbacks in open ones, and *vice versâ*. The defenders of each system have consequently striven to do away with the drawbacks adhering to their system, and in many respects with success. We will now go into this matter in detail.

Condensation of hydrochloric acid.—It stands to reason that the gas from the blind roasters is much more easily condensed than that from open roasters, hot as the latter is and diluted with a large quantity of fire-gas. The condensation of open-roaster gas is indeed impossible with the Woulfe's bottles, formerly general on the Continent; owing to this, in 1856 blind roasters were made compulsory by law in Belgium. Now-a-days we have got much beyond this. The bottles have been replaced entirely or partly by towers filled with coke, bricks, &c., and it has been recognized that the mainspring of all good condensation is the best possible *cooling*. If there is a sufficient cooling- and condensing-space provided, even the acid vapour from open roasters can be completely condensed. Indeed, whilst the former reports on the Alkali Act (up to 1867) seemed to show a much larger escape of acid vapours from open than from blind roasters, it was discovered that the latter lost a great deal of gas through leakages directly into the chimney which could not be detected by the inspectors, since they usually, up to the last few years, merely tested for any acid vapours remaining in the gas after passing through the condensers. Since this source of loss has been

more completely investigated, the reports actually show better condensation in the Tyne district, where only open roasters are used, than in the Lacashire district. The investigations of Dr. R. Angus Smith himself and of his colleagues have drawn the alkali-makers' attention to this source of loss; and the gratifying consequence has been much greater care in the construction of blind roasters. We must take it as established that there is no proof whatever of a more *complete* condensation of the gas from blind roasters; but it is certain that the gas is more *easily* condensed than that from open roasters.

Strength of the condensed acid.—In the case of blind roasters the roaster-gas is either condensed along with the pan-gas or in quite similar apparatus. If the cooling is sufficient and the supply of water properly regulated, nearly all the muriatic acid is obtained in the *strong* state; the liquid running away from the wash-tower only shows 1° or even 0° on the hydrometer. On the other hand, the gas from open roasters is condensed in separate towers; and formerly in this way merely weak acid, only fit for bicarbonate or for sulphur-recovery, was obtained, most of which was run to waste. Latterly, however, many works, by increasing their cooling-channels &c., have succeeded in obtaining a large portion of the open-roaster acid sufficiently strong to be employed, mixed with the pan-acid, for making chlorine. Thus the open roasters have partly made up for the start which the blind roasters had before them in this respect; but they will hardly ever completely do so—that is, permit the making of as much bleaching-powder.

Cheaper condensing-plant.—Undoubtedly, for an equally good condensation, much less condensing-plant is used for blind than for open roasters.

Employment of coals for firing.—Open roasters are mostly fired with coke, in order to avoid soot and ashes, less on account of the quality of the salt-cake, if this is used up at once, than because with coals, in spite of dust-chambers, the condensers would soon be stopped up and the disagreeable task of repacking them would occur very frequently. It is true that a greater absolute quantity of heat is required for a blind roaster; but although the effect of the direct flame in the open roasters is much greater, the deficiency is partly made up again by the more than double length of path travelled by the flame in a blind roaster. At all events the fuel of the muffles is cheaper. At few works only are open roasters fired

with coals, and only when no strong acid is wanted, as the soot must always be washed down by means of a strong jet of water in the condensers.

Saving of sulphuric acid for decomposing the salt.—Such a saving is undoubtedly effected by blind roasters against open ones, as will be subsequently shown in detail.

We now turn to the points in which *open roasters seem to have an advantage*—first of all to the *larger turn-out of sulphate.* This is indispensable. The calcination in an open roaster is much greater than in a blind one; the charge is always finished by the time the next charge in the pan is got ready, while with a blind roaster the pan-man must usually wait till the roaster-man has finished. Owing to this, a quarter or a third more sulphate is made in an open roaster than in a blind one; the pan also suffers less, as it has not to stand so many changes of temperature, which occur because the pan-man has to slacken his fire when waiting for the roaster-man. This seldom happens with open roasters; and consequently much more sulphate is usually got out of a pan before it cracks. The drawback in question can be avoided by putting two blind roasters to each pan, as shown in fig. 60; but this means a good deal more space, prime cost, and repairs.

Fig. 60.

A still clearer drawback of the blind furnaces is their *liability to need repairs.* This, indeed, is their weakest point. It is against the nature of a muffle to be made of very substantial brickwork, as it would conduct the heat too slowly and incompletely. The thin hollow bottom and the arch of a muffle suffer much more from wear and tear than the solid bottom and arch of an open roaster. Besides, any considerable repair of the inner arch can only be made after removing the upper arch, whether the latter wants repairing or not; the space between them must not be large

enough for a man to work in between, since, if it were, the flame would travel along the upper arch and would communicate but little heat to the lower one, that of the roaster itself. Latterly the scale has turned still more against blind roasters, since attention has been drawn to the fact that frequently acid vapours escape from the muffle into the outer flues, and thus get into the chimney without any condensation. Owing to this, the work has frequently to be stopped, and repairs to be made, long before the brickwork has suffered very much from the heat. Recently, however, by very careful construction and by employing very good material, blind roasters have been made to stand much longer and to keep much tighter; for instance, arches are made much tighter against gas by using specially moulded bricks, fig. 61, which are joined with a

Fig. 61.

very thin layer of fireclay mortar; thus the thickness of the muffle-arch can be reduced to $4\frac{1}{2}$ in., and a much better heating-effect can be produced. In this respect every thing depends upon the experience and skill of the manager, the mason, &c.

Greater security against the escape of acid vapours directly into the chimney.—As remarked before, this drawback of blind roasters has been only gradually discovered. Owing to this, the statements of the blue books are defective; for they only register what gas has been lost through the condensers, not that lost through the chimney or from any other cause. A loss of acid-gas may either take place from the pan or the roaster. In the former respect there is of course no difference between the two kinds of roasters, as they have the same pans; in describing these we see how this fault can be avoided in constructing and setting the pans. But the roasters behave very differently. In open roasters all gas passing through the furnace, both acid-gas and fire-gas, gets into the condensers. On opening the doors and drawing the charges some acid vapour may get into the working sheds; but this is very little; and as the workmen are the principal sufferers by it, they always do their best to avoid it. By fixing gas-hoods over the working-doors this loss may be reduced almost to zero, if

the hoods are not connected with the chimney, but with a separate small condenser made of stoneware pipes, say 2 feet wide and 20 feet high. In the case of ordinary blind roasters, however, there is always a stronger pull in the outer fire-flues than inside the muffle; consequently by the slightest crack in the arch a certain, often a large, quantity of acid vapour will get into the fire-flues and escape into the chimney, without passing through the condensers. Any cracks in the furnace-bottom are less dangerous, as these, being filled up by melting salt-cake, do not allow any gas to pass through; but sometimes whole tiles fall in and cause a great loss of gas. As the arch must always be thin, it is all the more liable to crack. Consequently, blind roasters can never be trusted, but several times daily the air of the fire-flues must be tested by aspirating a certain volume through distilled water and titrating with nitrate of silver. It is the best way to test, first of all, the main flue, if there is one, into which all the saltcake-furnaces lead; if this is found faulty, the furnace-flues must be tested singly, in order to find out the individual furnace at fault. Without this precaution large quantities of gas may escape unawares and may cause much damage and nuisance. Some persons believe they can form a sufficient idea of any loss of acid vapours from the appearance of the smoke issuing from the top of the chimney; but this is very deceptive, and not trustworthy, except for large losses.

Dr. Smith describes a case in which the fire-gas of the muffle had to pass through a separate wash-tower, in order to wash out any acid vapours casually escaping. A tower of 20 feet height and 8 feet square is said to have been sufficient for three furnaces. Such a tower, no doubt, must be packed with bricks very loosely, not to interfere with the draught, and consequently will not be very efficient for condensing the extremely diluted acid vapour passing through it; the two requirements of good draught and good condensation must clash with each other; and perhaps the arrangement was rather adopted *ut aliquid fieri videatur*.

In order to prevent the cause of the easy irruption of acid vapours into the fire-flues, viz. the larger draught in the latter, Muspratt has taken out a patent (May 4th, 1877) for a process analogous to that employed by Gamble for his gas-furnace, to cause an excess of pressure in the fire-flues, by dispensing with chimney-draught and, instead of this, forcing air underneath the

grate, also admitting more air in other parts of the furnace for burning the carbon monoxide.

Another patent (by Deacon) seeks to attain the same end simply by placing the fire-grate at a considerable depth below the bridge, thus causing a slowly ascending current of hot gas, which is checked by travelling round the muffle and thus exposed to a greater pressure than the gas inside the same. (See Appendix.)

Stronger sulphate.—Owing to the higher temperature of an open roaster, it is much easier to calcine the salt-cake and to decompose the common salt completely. In blind furnaces this can only be attained by employing a large area and consequently a very thin layer of material, and spending a good deal of time over the calcining process. This, of course, is much easier with furnaces possessing two muffles to one pan.

It is evident from the above that the circumstances to be regarded are very complicated; and frequently the choice between blind and open roasters is not very easy. The following seems to be pretty well established. Wherever it is necessary to get as much strong muriatic acid as possible, whether for sale or for generating chlorine, blind roasters should be employed; but they should be built as carefully as possible. Furnaces with two muffles are better than the single ones with respect to the quantity turned out. In this case there will also be a certain saving in the cost of condensers; but the flues ought to be daily tested in the manner indicated above. Where, on the other hand, the capital for condensers is a smaller consideration than the space for furnaces, and where it is not necessary to get all the muriatic acid, or where a portion of it is required in the weak state (say, for bicarbonate or for sulphur-recovery), there open roasters are preferable. In this case the manufacturer is much less dependent upon the skill of the furnace-builder. He has to take more care about the supply of water; but he need not fear any loss of acid vapours from his calciners. Contrary to the conclusions of the Belgian Parliamentary Commission of 1855 (in consequence of which blind roasters have been made compulsory in Belgium) and that of Freycinet (Annales des Mines, 1868, t. xiii. p. 153), it is the author's opinion that just in those cases where the first consideration is the entire prevention of the escape of acid vapours, open roasters are safer than blind ones, although they do not permit so much strong acid to be obtained.

The above will make it clear that, according to the circumstances of each special case, blind roasters or open roasters should be preferred; but even local customs have much to do with the choice. Blind furnaces are the only ones found in Belgium, where, as remarked, they have been made compulsory by law; but there we find Chandelon (Bull. Soc. d'Enc. 1871, p. 324) complaining of great carelessness about repairs; he frequently found furnaces with cracked arches in full work, of course with large quantities of acid vapour escaping through the chimney. In Germany and France, too, they are all but universal; and in Lancashire they are much more numerous than open roasters. The latter, on the other hand, are the only kind of furnace found on the Tyne.

A construction intended to combine the advantages of open roasters with those of closed ones is the *gas-furnace*, first proposed by Dr. Fletcher, and carried out in practice in several modifications in Lancashire, for instance by Mr. Wigg, of Runcorn. The gas, produced in Siemens's generators, is conveyed through an underground flue both to the calcining-furnace and to the pan; it is lighted, and the air admitted through five air-slides in the front end of the furnace. The method employed for heating the pan is a very rational one. The flame issues below its centre, and is drawn off by four flues, so that it spreads quite equally; it can be regulated at will by opening or closing the gas- and air-dampers much less than for a direct fire; and with the gas-fire the pans are much less liable to breakage. The calcining-furnace is heated by a separate gas-flue, first indirectly, through the flags forming its bottom; the flame returns over the bottom and heats the charge upon it directly. From this, however, arise several drawbacks, which have caused the system to be abandoned again in some cases. In the first place, the furnace is too long, and the flame, which has already travelled underneath the bottom a distance of 30 feet, in order to return over the same, cannot bring more than a fourth or at most a third part of the furnace-bottom to a heat sufficient for finishing the sulphate. This can be avoided by making two beds of 15 feet length each, assigning one of them to each pan. But even then the sulphate easily fluxes through the joints of the plates and stops up the flues underneath. This happens much more readily than with ordinary blind roasters, because here the flame travels first over the arch and then under the bottom, which thus does not get so hot. The object of the whole was

this—to produce, by means of the gaseous fuel and the regulation of the air, a flame quite free from smoke and not containing a large excess of air, which was to permit the production of as much strong muriatic acid by a reverberatory furnace and a coal fire as with a blind roaster; but this has not proved to be the case; and Wigg's furnace has consequently not been widely adopted.

Another gas-furnace has been constructed by Gamble; this is

Fig. 62.

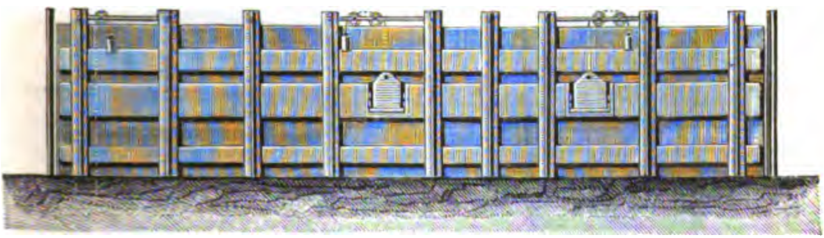
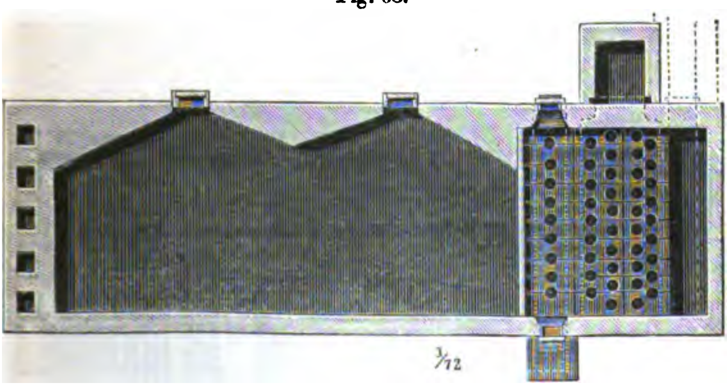


Fig. 63.



represented in figs. 62 to 66. Here an ordinary blind roaster is fired by means of gas-producers; the air required for combustion is heated by passing through a system of iron pipes, which, on their part, are heated from the outside by the waste heat of the furnace-fire. The greatest drawback of blind roasters, the escape of acid vapours, through any chinks, from the muffle into the fire-flues, is to be avoided by carefully adjusting the dampers so as to

put the gas in the generator under a somewhat higher pressure than the gas inside the muffle. This is not very easy, since the pressure inside the muffle varies considerably, according to the rate at which acid vapours are given off; but with a little care the

Fig. 64.

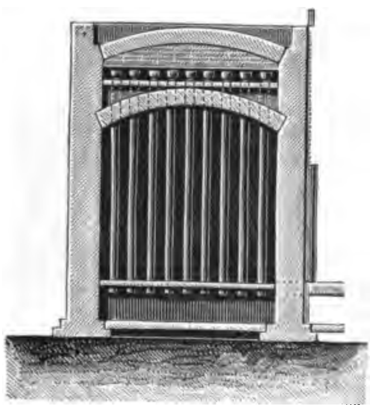


Fig. 65.

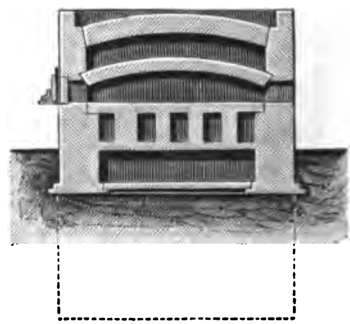
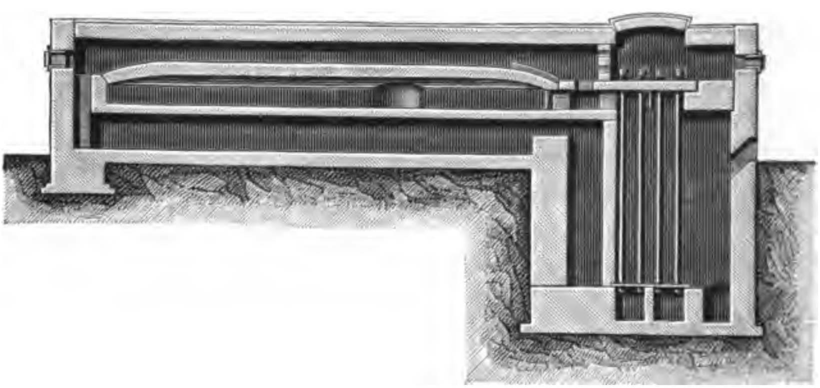


Fig. 66.



object can be attained. At Messrs. Gamble and Sullivan's these furnaces are working very well, and there is not the inconvenience of gas getting into the fire-flues; if there are any cracks in the

arch, the fire-gas rather enters into the muffle, but not *vice versâ*.

The following rules hold good for all sulphate-furnaces. It is advisable to paint, not merely all the metal parts, but the whole of the brickwork outside, with hot coal-tar, and to repeat the painting when the furnaces are hot. Thus both the iron and the brickwork will be protected against the rapid corrosion to which they would both be subjected by the muriatic acid vapour. Thus protected, an open furnace goes a long time without any important repairs, except occasionally renewing the lining of the fireplace. But, in the nature of things, the muffle of a blind furnace cannot but require frequent repairs: in the first place, it must be very thin, so as to be more readily penetrated by the heat; secondly, its outside is acted upon by the fire and its inside by the acids; the bottom moreover, is injured by the mechanical labour of turning over the sulphate; thirdly, even the smallest crack must not be neglected, but the furnace must be stopped in order to repair it, so as to avoid losses of acid vapour. Consequently it is much better not to place the acid-gas flues on the top of the arch, but sideways, as shown in figs. 42 and 44 (pp. 79 and 80).

In regard to the brickwork of the pan, the lining of the fireplace and the arch over the grate suffer rather much if the work is pushed hard, and must be pretty frequently renewed. The upper part (or, in case of heating by waste heat, the whole) of the fire-flues suffer very little. The arch over the pan, if built independently of it aud well constructed, may last out several pans.

Mechanical Saltcake-Furnaces.

The first of these that came into actual operation was that of Jones and Walsh (patented in 1875). With this there is no separation into two stages, but the whole operation is carried on in a large shallow cast-iron pan exclusively heated *from the top*. Thus the great drawback of the ordinary pans heated from the bottom (the frequent breaking) is avoided; and whilst with those every thing depends upon the skill, sobriety, and goodwill of the attendants, the new furnace is independent of them. It is only possible to work a furnace of this kind by substituting for the turning over by hand that by mechanical contrivances; this permits finishing the operation in the same vessel, while the salt is

decomposed more completely and at a lower temperature. Figs. 67 to 69 represent the original construction. The furnace con-

Fig. 67.

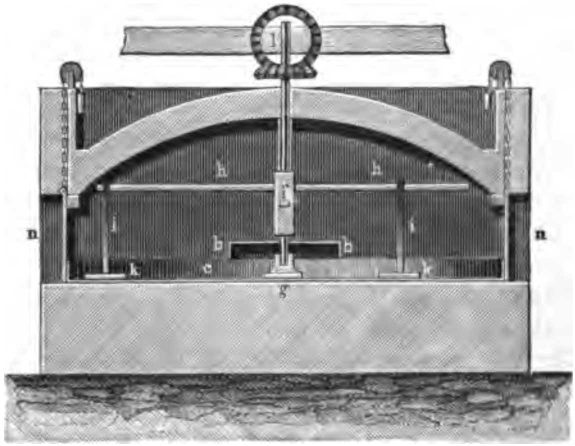
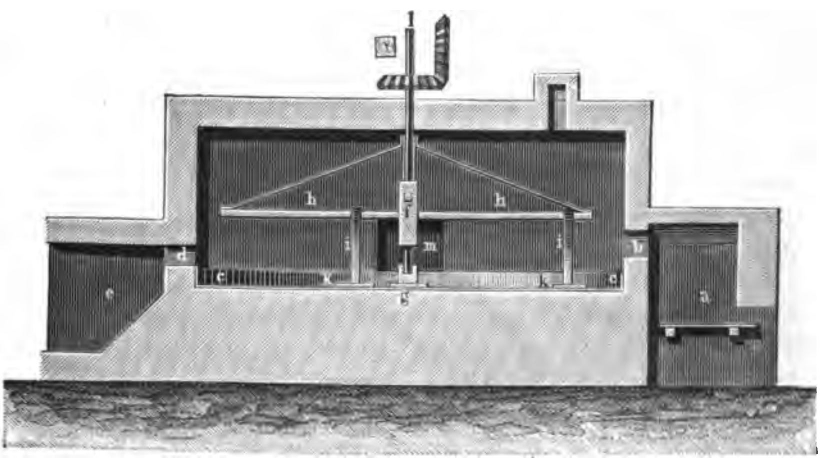


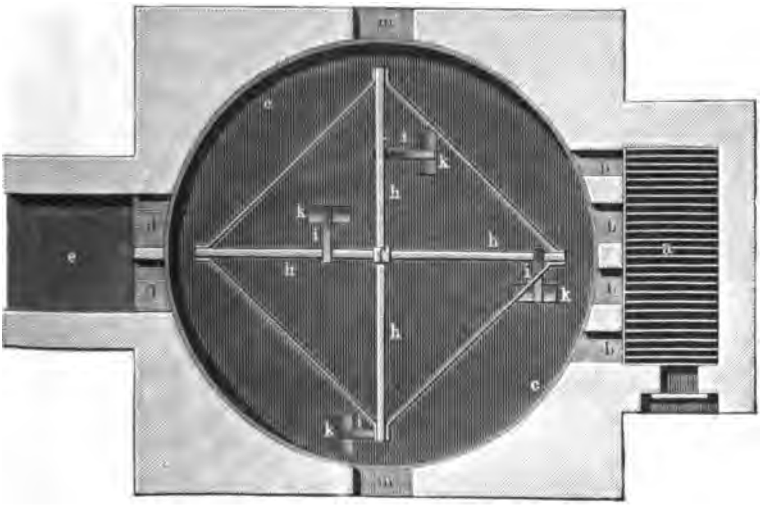
Fig. 68.



sists of a circular pan, *c*, 14 feet wide, with a flat bottom and a 6-inch flange, resting on solid masonry and heated from the top

by a coke fire. In the centre of the pan there is a footstep, *g,* in which an upright shaft, *f,* revolves once every $2\frac{1}{2}$ minutes; the shaft passes through the pan-arch, and is driven round by toothed gearing, *l.* Four strong horizontal arms, *h,* are fixed to the shaft; and to these the slanting rods *i,* with the scrapers *k,* are attached

Fig. 69.



by cotters. The scrapers are arranged at different distances from the shaft, so that the whole pan is ranged over by them. They are the only metal parts subject to much wear and tear; but this amounts to less than that of the ordinary pan and furnace-tools; and the scrapers can easily be replaced. The shaft is driven by a steam-engine with a 5-inch cylinder. *a* is the fireplace; *b,* the snore-holes, through which the fire gets to the pan, *c*; it escapes through *d* into the flue *e,* leading to the condenser. The openings *m,* usually closed by doors *n,* serve for charging and withdrawing.

This construction was found capable of improvement in more ways than one; and several new furnaces were made according to the plans of Mr. Goodman of Newcastle; these improvements are shown in figs. 70 to 72. The fireplace is put to one of the buttresses of the pan-arch; so that the latter can be kept much lower

Fig. 70.

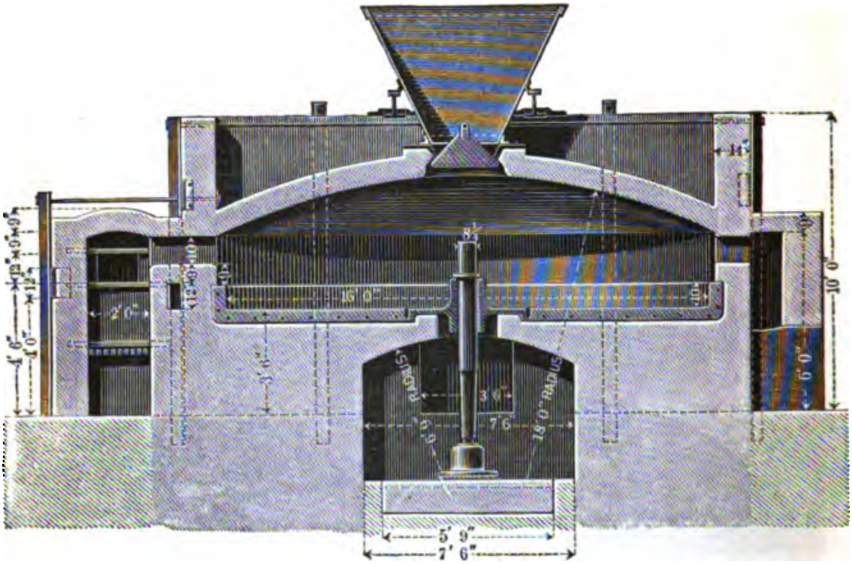


Fig. 71.

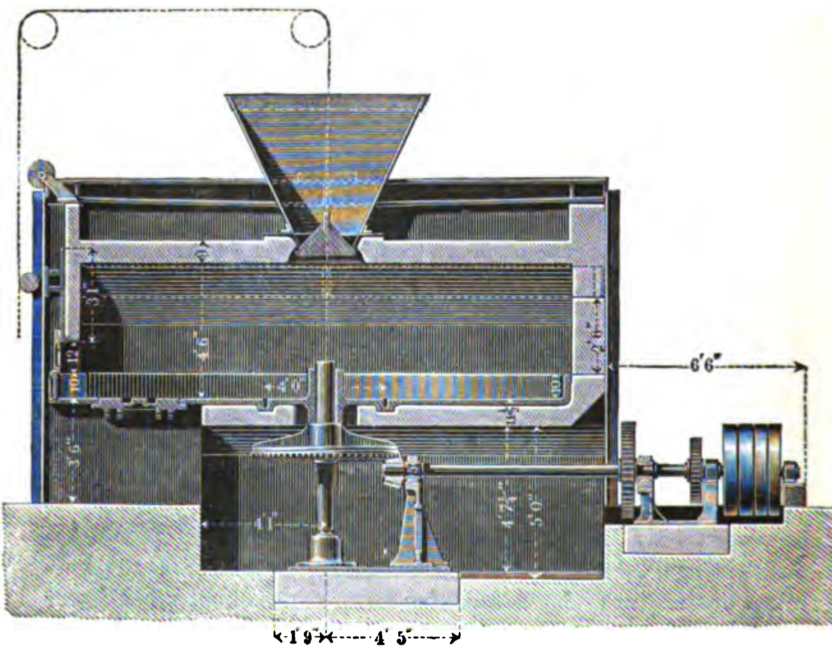
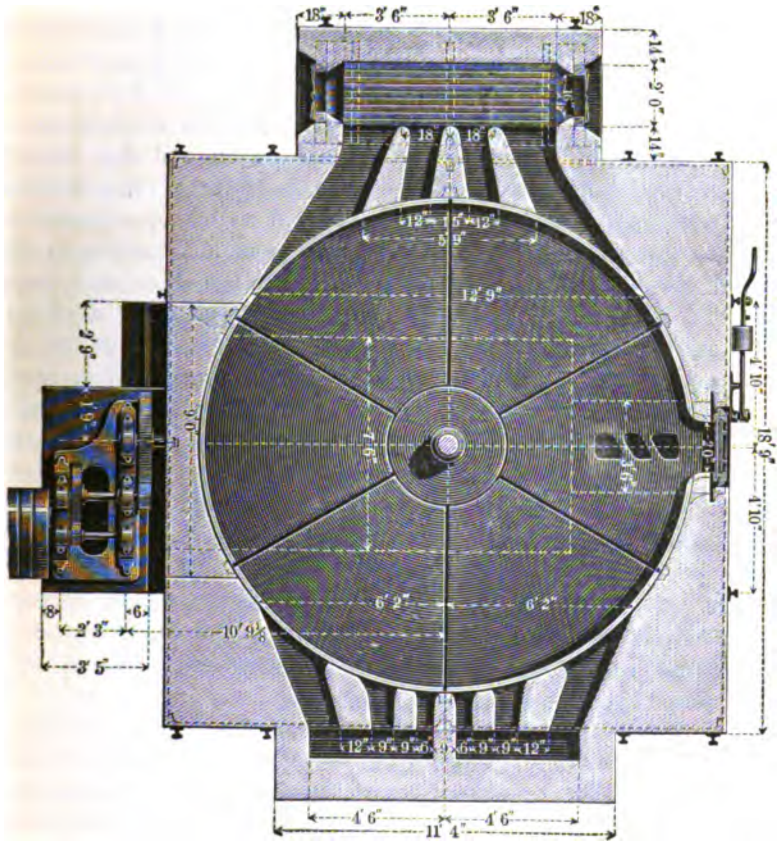


Fig. 72.



down. The pan is made 16 feet wide, and placed on an arch; the shaft is driven from below. The scrapers are replaced by cast-iron ploughs, which ordinarily only turn over and mix the contents of the pan, but, on reversing the gearing, serve for conveying the stuff to the circumference and discharging it there. The pan-arch is surmounted by an iron hopper, closed by a balanced cone, which contains the whole charge of salt, viz. 5 tons, and, on lifting the cone, allows it to drop at once into the pan. Thus both the time and the labour of charging and discharging are reduced to a minimum.

The smaller pans only hold 3½ tons of salt; and the shovelling in through the working-door takes about an hour. Then about

four fifths of the acid is run in by two lead pipes ending just over the pan-edge. The salt and acid are quite regularly mixed, and there is no tendency to boiling over; no tallow is necessary to prevent this. The evolution of muriatic acid gas, which in the ordinary pans is very tempestuous during the first quarter of an hour and thus puts a great strain on the condensers, in Jones and Walsh's furnace is much more even, and the condensation accordingly easy and complete, in spite of the dilution with air. After the mass has been stirred round for a quarter of an hour, a sample is taken out and tested; and, according to the results of the test, more acid is run in, or, on the other hand, more salt can be added. Just this possibility of improving a charge during the operation is an important advantage. Owing to the intimate mixture, about 5 per cent. of sulphuric acid is saved upon the ordinary open process. The heat in the furnace is only 425° C. against 650° C. or upwards in the ordinary open roasters. Each operation takes about 5½ or 6 hours. The sulphate appears as a finely powdered mass, quite free from lumps and very pure; two samples taken by the author himself showed 0·6 and 0·2 per cent. respectively of free acid and 0·58 and 0·12 per cent. respectively of free salt. One man can easily serve one furnace, and also wheel all the salt, against two panmen, two or four roastermen, one weighman, and one salt-wheeler in the ordinary process.

The hydrochloric acid would in this case seem to be very difficult to condense in a strong form, since the sulphate is exclusively made by direct top-fire. But it is not so, nevertheless, no doubt owing to the very even evolution of the gas and to the much lower heat. At Messrs. Jones's works the acid vapour, mixed with the fire-gas, first passes through a fire-brick flue 3½ feet high, 2½ feet wide, and 50 feet long (cast-iron pipes would cool it much better), then through a "shower-bath," consisting of a stone trough, whose top is provided with about 80 water-lutes; a 1-in. water-pipe with many small holes causes a fine spray of water constantly to meet the gas, cooling it and precipitating the smoke, without condensing much acid, because the time of action is too short. The water continually runs off at half the height of the tower; it shows about 1° Tw. Then the gas passes into an ordinary coke-tower 7 feet square and 50 feet high; the acid running off is 28° to 30° Tw. strong. The *quantity* of the acid condensed does not seem to have been exactly determined; but the condensation is good, and only

0·2 grain HCl per cubic foot of air can be detected. There is no nuisance whatever from gas escaping through the doors, or after drawing the charges; and a frequent source of nuisance in the ordinary furnaces, the damper between the pan and the roaster, has no existence here.

Afterwards, however, several drawbacks of Jones and Walsh's furnaces were discovered, which had been overlooked at first. Thus the cast-iron ploughs have not proved successful, and wrought-iron scrapers have been re-adopted. There has also been a difficulty in keeping the joints of the pan-segments tight; and altogether the necessary repairs are frequent and costly. A recent patent of Messrs. Jones and Walsh (May 5th, 1877) seeks to overcome one of these difficulties by introducing an improved form of flange, with peculiar expansion joints. The furnace certainly does not turn out as much work as had been expected, viz. at most 12 tons daily with loosely packed condensers, which do not allow any very strong acid to be obtained, and only 5 tons with closely packed coke-towers.

These matters have been ventilated fully in a paper read by Mr. Jones to the Newcastle Chemical Society, and in the subsequent discussion (Chem. News, xxxv. p. 51). Jones attributes the undeniable want of success of some of the mechanical furnaces to two causes, viz. insufficient heat and unsuitable modifications in the construction of the furnace. The former, in some instances, was caused by the furnace-arch being made too high above the pan-bed. It has been found in practice that a temperature of 440° to 555° C. is required to work off a batch of saltcake in a reasonable time; where the arch of the furnace has been built 4 ft. 9 in. or 5 ft. above the bed, it is difficult to get the requisite degree of heat; consequently the charge takes two- or threefold the time for finishing, thus causing loss of time, labour, and fuel. Insufficient draught through the condensers has in other cases prevented the furnace from being properly heated. This was still more the case when a double arch was tried, as in an ordinary blind roaster, for keeping separate the gases from the fire and those from the charge. As far as the details of construction are concerned, the ploughs rigidly fixed to the cross arms have not been found to answer so well as the loose scrapers or paddles, partly owing to the caking of the salt-cake on the sole of the pan. The best form of stirrer to prevent this, and at the same time thoroughly to expose the charge to the heat, is still a desideratum; so far nothing has been found

to work better than the original scrapers or paddle-blades attached to the cross arms by a wrought-iron shank, with a bolt-and-eye arrangement. The greatest change has been the abandonment of cast iron and the reversion to the original construction of wrought iron in those portions of the machinery exposed to the full heat of the furnace. It has been found that the cast-iron parts, after exposure for some time to the heat (and the acid vapours), become extremely brittle and break down with a slight strain; only in one establishment on the Tyne has this been overcome by a special combination of metal; and the cast-iron working parts there have been a complete success.

The vertical shaft is now made of 7-in. solid round wrought iron, and the cross arms 5 in. square; and this construction has stood the test of practice very well. The pan is now made 12 in. deep and has two doors at opposite sides; in a pan of this depth and of 16 ft. diameter a charge of 6 tons of finished sulphate can be made. In order to get the arch lower and bring the heat more directly into contact with the charge, the roof of the furnace is supported upon flat metal girders for about one third of the diameter at each end, leaving a space of about 6 ft. in the centre covered by a brick arch, so as to allow space for the working of the diagonal stays which attach the cross arms to the vertical shaft. Open passages 18 in. wide are now left in the brickwork, going across from side to side under the joints of the pan; thus any leakage which may occur can be seen and remedied at once without any stoppage of the furnace. The wear and tear of the pan itself is very small; a pan taken out after 18 months' continuous use was found to be in perfect order. The use of *hot* sulphuric acid of 140° Tw. conduces to the safety of the pan, and is found to expedite the finishing of the charge.

The consumption of coke has averaged about 2½ cwt. per ton of finished sulphate of soda, and about 3 cwt. per ton with sulphate of potash.

Mr. Jones considers that the following points have been established:—

1. The nuisance arising from the escape of vapours from the furnaces or from the batches of salt-cake has been almost entirely overcome.

2. The condensation is effectually performed, and the muriatic acid recovered at a strength varying from 24° to 30° Tw. (The

chimney-tests showed an escape of 0·10 to 0·15 grain HCl per cubic foot.)

3. The finished sulphates are of a superior quality and of a more uniform character.

4. Allowing for the extra cost of coke (as against coal where used), steam, &c., a material saving in labour, in wear and tear, and also in sulphuric acid is effected as compared with the manual-labour system of decomposing. (At Messrs. H. L. Pattinson & Co.'s works there was used upon 100 parts of real salt in the hand-furnace 90·00, in Jones's furnace 85·80 SO_4H_2, against the theoretical quantity of 83·76, showing a saving of 4·2 per cent. SO_4H_2 by Jones's furnace.)

There is at least one half of the manual labour saved; ordinary day-labourers, instead of skilled men, can be employed; and there is no necessity to depend upon their goodwill to prevent the breaking of pans.

In the discussion following upon Mr. Jones's paper, the present manufacturers on the whole upheld his statements; one of them mentioned that only after introducing the Jones furnace had he succeeded in bringing down the escape of acid vapours within the minimum prescribed by the law. The maximum quantity turned out in 5½ days was stated to be 75 to 80 tons of sulphate from salt alone, or 100, even up to 103 tons, when working nitre-cake and salt together.

Special inquiries made by the author in 1878 elicited reports not quite so rose-coloured. The maximum quantity obtainable in 7 days was stated to be 50 tons; and perhaps on this account the quantity of fuel (inclusive of steam) was said to *exceed* that used in the ordinary hand-furnaces. Most complaints were made about the enormous amount of repairs entailed by the machinery: cast-iron shafts break; and wrought-iron ones twist. Mr. Jones certainly declares this to be entirely owing to faulty workmanship, and asserts that in substantial and well-constructed furnaces the wear and tear is less than in the hand-furnace and roaster.

A large portion of the evils experienced with Jones and Walsh's furnace is no doubt to be accounted for by the fact that the matter was pushed on too fast, and that the manufacturers adopting it added on their own part "improvements" which did not turn out to be such; at least the furnaces erected by the patentees themselves in a few places seem to go on comparatively well. It must

also be noticed that the worst drawback of that furnace, its great liability to breaking down, appears to be largely diminished, if the large turn-out, certainly promised by the inventors, is given up and a weekly make of 40 to 50 tons only is aimed at. The furnace in this case need not go so hot, and consequently the machinery does not suffer to any thing like the same extent, as when the work is pushed on so fast.

A new patent taken out by Jones and Walsh (dated May 5th, 1877) seeks to avoid the objections made to their furnaces by a radical cure. They adopt the principle long proved to be right in metallurgical operations and quite recently in Mactear's patent calcining-furnace, viz. fixed stirring-gear along with a revolving pan serving as furnace-bottom. The pan consists of an outer part of wrought iron and an inner one of cast iron; it revolves in a footstep below on a spindle passing through the pan and protected against the chemicals by a collar attached to the pan itself. The lower edge of the pan is provided with annular toothed gear, by which it is made to revolve; the upper edge with a depression running all round it and forming, with a ring reaching down into it from the fixed furnace-roof, a sand lute, which does not allow the outer air to get in or the fire and acid gas to get out. The charging and discharging of the pan takes place by means of a ladle, which is lowered down to the bottom of the pan in a slanting position and left there fixed whilst the pan is revolving, so that the sulphate is pushed into the ladle. (This process has not been carried out yet, and seems to have been patented merely to cover the ground.)

No statements have been published on the exact *amount of hydrochloric acid* obtained in Jones's furnace. The author is able to supply such from the works of Messrs. Vorster and Grüneberg, of Cologne, who make 7½ tons of potassium sulphate per 24 hours in such a furnace. As the potassium chloride employed already contains 10 to 15 per cent. K_2SO_4, the theoretical yield of acid, on the K_2SO_4 obtained, only amounts to 36 per cent. Instead of this were obtained at first, in summer, 5895 kilog. acid of 30° Tw. = 1691 kil. HCl = 22·5 per cent., in autumn 6550 kil. of 31° Tw. = 1945 kil. HCl = 27·3 per cent. on the sulphate. The quantity has quite recently risen to 7500 kilog. acid, half 32°, half 29° Tw., say 2175 kilog. HCl or 29 per cent. on the K_2SO_4, against 36 per cent. required by theory; this is a very satisfactory result (comp. Chapter VIII.).

In spite of all the drawbacks mentioned and of decided imperfections in the furnace of Jones and Walsh, it is a fact that mechanical furnaces for decomposing salt are already now successfully at work, both in England and Germany, and that they at any rate save a good deal of labour and a considerable percentage of sulphuric acid (especially if employed pretty strong), and turn out a very good quality of sulphate. Indeed, in 1878, new furnaces of this kind have again been ordered for several works. Altogether up to the autumn of 1878 about 30 of these furnaces had been erected, of which, however, about one third had been abandoned again, owing to the circumstances mentioned above.

A patent of Black and Hill (dated June 14th, 1877) is intended to avoid the drawbacks of Jones and Walsh's furnace by reverting to the principle of carrying on the operation of decomposing in two separate stages. The pan heated from above and provided with revolving stirrers is essentially retained; but only that function is left to it which belongs to the calcining-furnace or roaster of the ordinary process. The first action of the vitriol on the salt takes place in a special apparatus, also provided with stirring-gear, but heated from below like an ordinary decomposing-pan. The salt is to be employed dry, the acid as strong as possible, and both heated by the waste heat of the apparatus. The latter is represented by figs. 73 to 75. Fig. 73 is a side sectional elevation, fig. 74 an end sectional elevation, fig. 75 a sectional plan. A is a cast-iron trough set in the brickwork B, and provided with a brick roof; it is heated by the waste heat of the furnace I, circulating in the flues C C. On the top there is a man-hole *a* for charging the salt, a pipe *b* for running in the vitriol, and a pipe *c* for the escape of muriatic acid gas; the openings *d d'* closed by slides serve for the discharge of the batch when it has attained a proper consistence. The contents of the trough are agitated by the stirrers D secured to a horizontal shaft E, having its bearings at *e e* within the cylinder, so as to obviate the necessity of stuffing-boxes in the ends. The rotary motion is imparted to the shaft E by means of the gearing *f*, the vertical shaft F, extending through the top of the cylinder, and of bevel gearing *g* from another horizontal shaft G which is supported in bearings *h h* and carries on a driving-pulley H. The trough A is about 11 ft. long, 5 ft. 6 in. wide, and 4 ft. 6 in. deep. The charge consists of from 2 to 5 tons of salt along with the calculated quantity of sulphuric acid. First of all the sulphuric acid

Fig. 73.

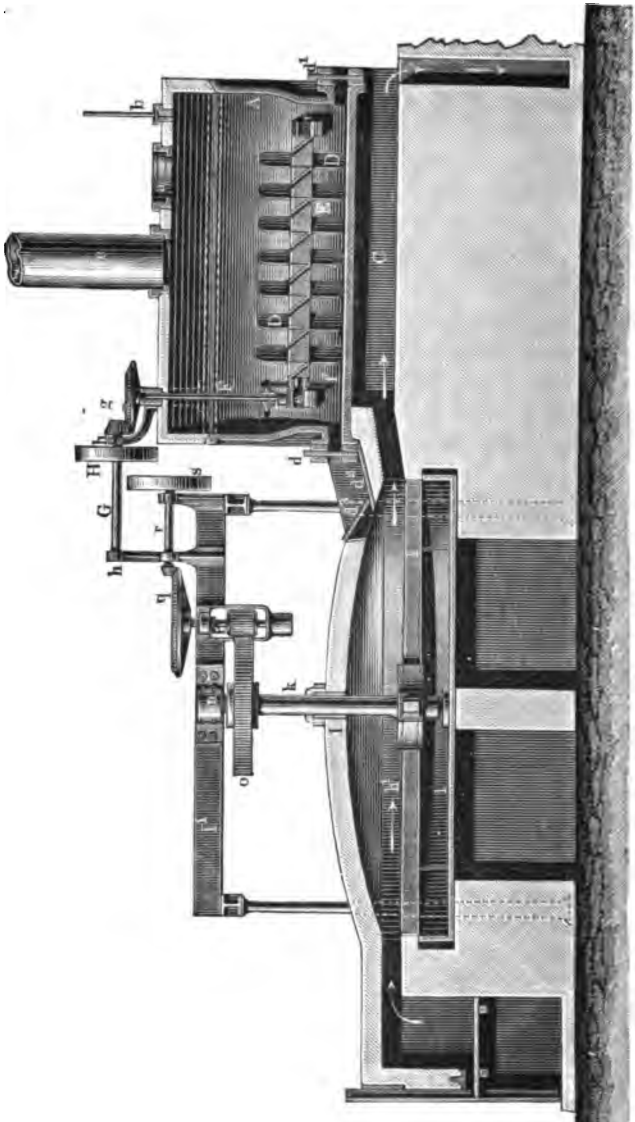


Fig. 74.

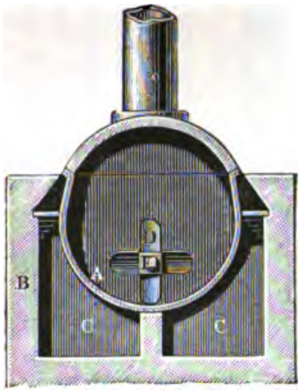
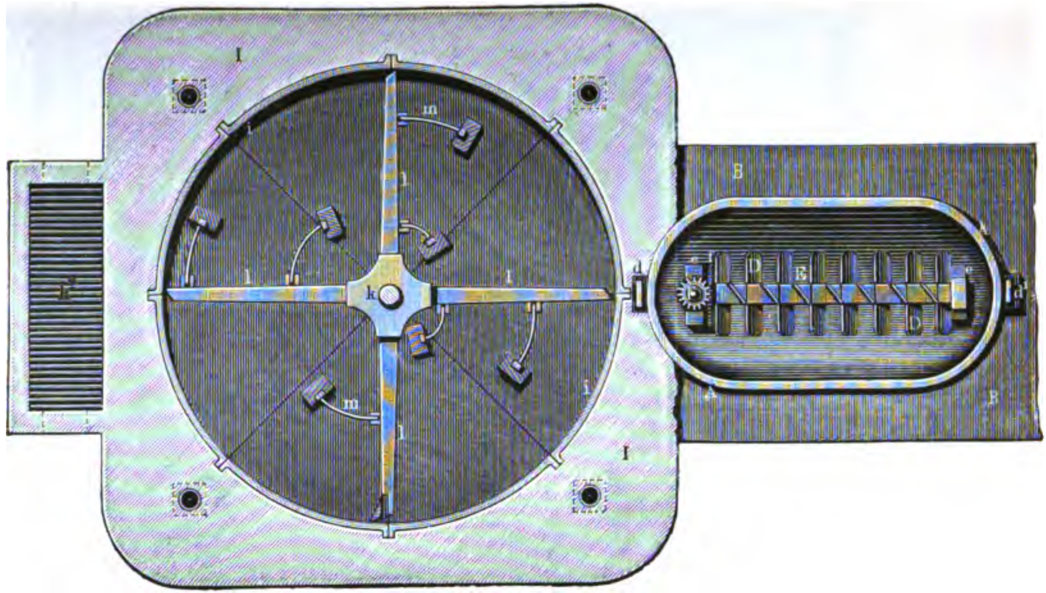


Fig. 75.



is run in; then 70 to 80 per cent. of the salt is added, and at the last moment only the remaining 20 to 30 per cent. of salt. Thus the mass remains more liquid, which is favourable to rapid evolution of the hydrochloric acid gas, and moreover prevents the charge from adhering to the cylinder. If it is intended to get as much work as possible out of the apparatus, the trough A should not be heated by the waste heat of I, but by an independent fire.

The trough A is placed at about three feet above the level of the finishing-furnace I, and so that their edges are nearly at the same perpendicular. When the contents of the trough have attained a suitable consistence, the slide *d* is drawn and the charge is allowed to flow through a shoot d^2 (also fitted with a slide d^3) into the finishing-furnace. This consists of a chamber h', heated by a fire at h^2, and containing a fixed circular bed or trough *i*, in the centre of which is arranged a vertical revolving shaft *k*, having arms *l* with scrapers *m* attached to the shaft, which is suitably supported at its lower end by the bed and at its upper end by a bearing at *n*, and which is driven by means of the gearing and shafts *o p q r s* from the engine. This construction was expected to effect a larger production, a saving of fuel and of acid (because only at the end is the latter exposed to the direct action of the fire), and better condensation and stronger hydrochloric acid (owing to the employment of a closed trough heated from below and the avoidance of leaks through bottom-joints). Only longer experience on a large scale would be able to decide whether these advantages are not outweighed by the multiplication of machinery and the difficulty of maintaining this in proper order, especially in the trough A, where it is in contact with acid. So far the improved furnace does not seem to have commanded as much success as was expected by its inventors.

Another mechanical furnace has been patented by Cammack and Walker (March 3, 1876). It is extremely ingeniously planned, but can hardly, it seems, be carried into practice with the mechanical means at our command. Its principle is that of a tube into one end of which the salt is introduced mechanically, along with the vitriol, and moved forward along the tube, to issue at the other end as finished sulphate, the hydrochloric acid being given off in a perfectly even, continuous current. The apparatus (figs. 76 to 79) consists of a cast-iron cylinder, 1, about 20 feet long and 3 to 4 feet wide, supported at each end on rollers, 2, and enclosed in the

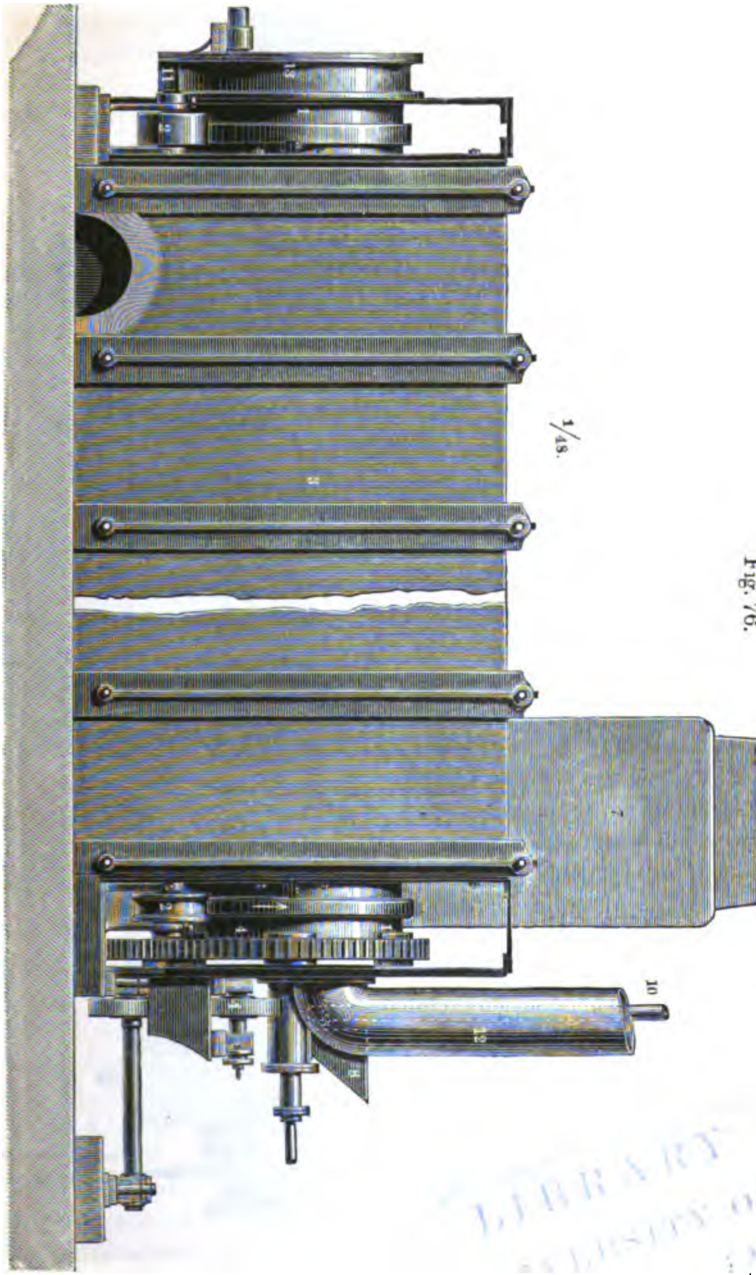


Fig. 76.

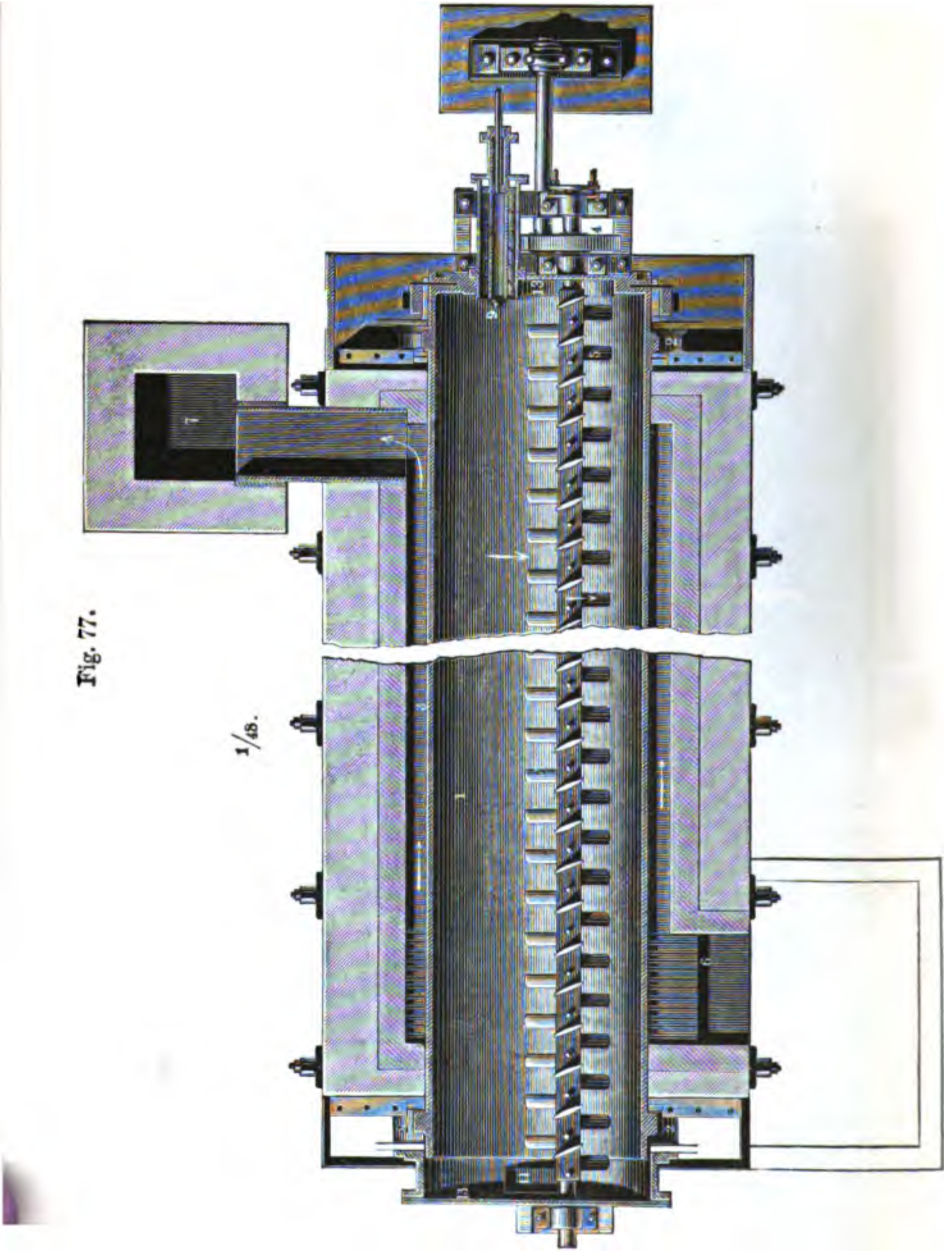
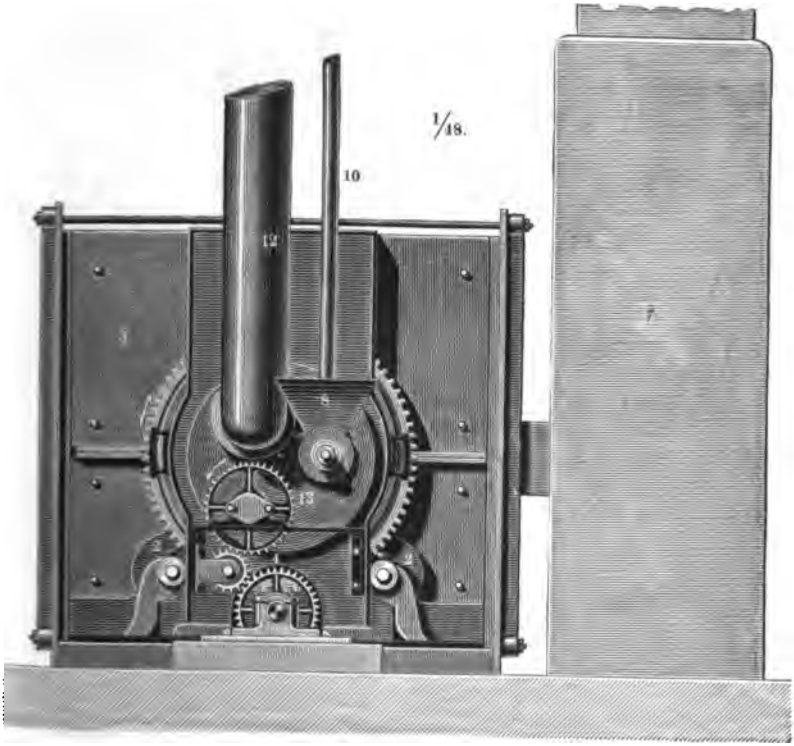


Fig. 77.

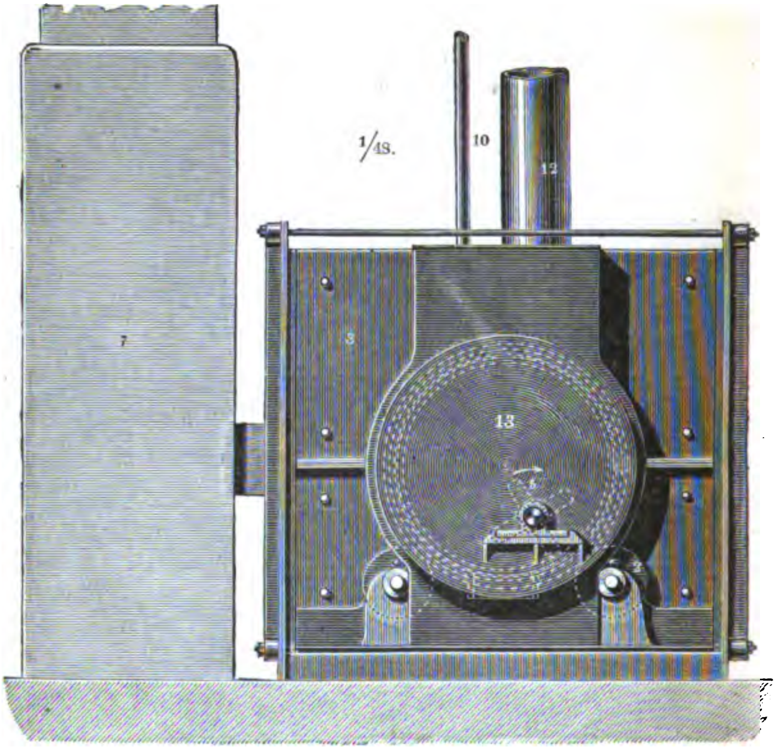
1/48.

Fig. 78.



furnace, 3; 4, driving-gear for causing the cylinder, 1, and also the scrapers or agitators and bar, 5, to revolve; 6, fire-grate. The products of combustion pass in the direction of the arrows to the uptake 7; 8, hopper, from which the salt is supplied to the cylinder by means of the worm 9; 10, inlet pipe for sulphuric acid; 11, outlet for the finished salt-cake; 12, waste-gas exit. The salt and acid arrive already perfectly mixed in the cylinder. This, besides the shaft shown in the drawing, contains another, longitudinal, stationary shaft, provided with teeth which scrape the sides of the cylinder on its rotation, and which are intended to prevent the caking on of the stuff. The other shaft (5) revolves in the opposite direction to the cylinder; this also is provided with teeth or stirrers, so placed that they continuously move the mixtures towards the outlet 11. The hydrochloric acid gas is taken away by the pipe 12 into a series of 12-inch glass pipes, where it is con-

Fig. 79.



densed by water in the form of a spray. As it is almost pure HCl, free from fire-gas and air, 50 feet of such pipes are said to suffice for complete condensation. Such a cylinder was to furnish daily 8 tons of salt-cake.

This very interesting furnace was erected by Messrs. Golding and Davis at Widnes, but was soon discontinued again, because the mechanical difficulties could not be overcome. The two shafts inside the cylinders, for which no intermediate bearings can be provided, soon sagged under the influence of the heat. Owing to this the teeth and scrapers did not work properly; the mixture, instead of evenly moving along the cylinder, stuck fast to the sides of the cylinder and stopped it up. As, however, this furnace would be extremely favourable for Deacon's chlorine process, that firm has taken it up again; the result of their experiments so far is not known.

The process with cast-iron decomposing-pans is distinguished from that which is carried on in lead pans principally by this—that it can be accomplished much more quickly, because greater heat can be employed and there is no fear of the tools injuring the pan. Working for a large turn-out is consequently possible with cast-iron, but not with lead pans.

The pans, after moving their contents into the roaster, must be cleaned from crusts as much as possible; to purposely leave them in the pan, as is prescribed in some places, is a grave mistake; for in the unavoidable interval up to the introduction of the new batch such crusts burn fast, and cannot be dissolved again, causing the pan to crack before its time. Nearly all cracks in pans can be traced to the formation of crusts through unskilful or negligent work—except such as are owing to faults in casting, to bad setting, or to fair wear and tear; the former will come out almost immediately after starting a new pan, the latter only after a long time. After removing the crusts the pan is allowed to cool down a little, by opening the fire-door or by shutting off the gas in the case of gaseous fuel; in any case the pan must cease to be red-hot, else it will suffer from the cold, damp salt, and even more from the vitriol; at the best the evolution of hydrochloric acid will in this case be much too violent and cause the pan to boil over, blowing off gas through all the joints, and rendering the condensation incomplete. In small works it may be possible to do as some advise—dry and heat the salt before charging; in large works this would be too troublesome, and the salt is nearly always put into the pan direct from the warehouse, with its natural moisture, usually varying from 2 to 7 per cent. according to circumstances. It is mostly shovelled in at the working-doors. Hoppers for charging from the top are not frequently found, both because they much increase the weight upon the arch, and because the pan-men have at any rate time for that work. Besides, the pan-bottom is cooled too quickly if the whole mass of salt is suddenly let down into it; and in this case, at least, the vitriol ought to be heated pretty strongly and run into the pan *first*. It will not do to rely upon the salt sufficiently drying and heating within the hopper in the interval before the next operation. Usually there is a metal plate in front of the working-door, and the quantity of salt weighed off for each charge has previously been laid down upon this plate against the pan-furnace, so that nothing is left to do but to shovel it in.

The quantity of salt taken for each batch varies very much in different works. Batches below 5 cwt. of salt are as rare as those above 10 cwt. for open roasters, or 16 cwt. for close roasters (in the latter case taking twice as much time). The usual quantity in English works is 8 or 9 cwt. for open roasters, 14 to 15 cwt. for close roasters; on the continent, where close roasters are all but universal, mostly smaller batches are made—for instance, at Aussig 12 batches of 8 cwt. each in 24 hours, at Stolberg 8 batches of 6 cwt. each in 24 hours.

On the purity and concentration of the *sulphuric acid* we have already said what is needful (see p. 42), and also in reference to its measuring, heating, and running in (see p. 70). As to the temperature of the vitriol, manufacturers are not agreed. It ought never to be below 50° C.; but some have it upwards of 100° C. For the pan, the hotter the sulphuric acid the better; but if it is too hot, the hydrochloric acid is given off too fast, with the consequences previously described; there is always, therefore, a medium to be observed. The temperature ought to be always approximately the same, in order to regulate the *quantity* of the vitriol—which is always measured, and whose volume is considerably altered by great changes of temperature; corrections for these would make the measuring very complicated, in connexion with the unavoidable corrections for differences in the strength of the sulphuric acid and the degree of moisture of the salt. Usually the latter is tested once a day in the laboratory, and special tables enable the workmen to reduce the quantity indicated to them to that corresponding to the strength of acid they may happen to receive from the chambers.

The absolute quantity of sulphuric acid would, according to theory, amount to 49 SO_4H_2 with 58·46 NaCl, or to 83·81 per cent. of real sodium chloride. As acid of 144° Tw., measured at 15° C., contains 78 per cent. SO_4H_2, 100 parts of real NaCl answer to 107·44 parts of vitriol of 144° Tw. Now real NaCl is never employed; for instance for a 95-per-cent. salt the requisite quantity of acid would be 79·62 per cent. of SO_4H_2, or 102·07 per cent. of acid of 144° Tw. In practice somewhat more acid must be employed, especially if saltcake for alkali-works has to be made; but other cases may occur as well. If, for instance, the saltcake is to be as strong as possible, more than the theoretical quantity of vitriol must be taken; for as it is impossible, at least in hand-worked furnaces, to mix all parts exactly and instantaneously, a

little sulphuric acid will already be volatilized in some parts of the mixture, where it is in excess, whilst undecomposed common salt remains in other parts. If, therefore, the percentage of salt is to be 1 per cent. or below, a little more vitriol must be employed, say 1 or 1½ per cent. calculated as SO_3, in addition to that volatilized with the hydrochloric acid vapour.

Some of the largest manufacturers assume, in the calculation of the sulphuric acid produced at their works, which is not measured directly, that for each 100 parts of salt of usual moisture, say 5 per cent., 81·33 parts of SO_4H_2 are employed for making strong sulphate in open roasters. In the same case the author himself has found 82 per cent. necessary; and he has obtained from other factories the figures 82·5 per cent. for open, and 79·3 or 80·8 per cent. for close roasters.

If, on the other hand, the sulphate is required to be entirely *free from acid*, for this very reason rather less than the theoretical quantity of vitriol must be employed, so that 2 or 3 per cent. NaCl remain in the finished product. This should not be done for making alkali.

In any case a larger excess of vitriol is used in open than in close roasters—in the former often 5 to 7 per cent. above the theoretical quantity, because the greater heat and the direct draught carry away a portion of it before it has had time to act upon the salt, whilst the excess required for the slower work in blind roasters only amounts to 2 or 3 per cent. The statement of Wright (Chem. News, xvi. p. 17) is anyhow exaggerated, according to which the average loss of vitriol in open roasters would be 12·6 per cent., that in blind roasters 2 per cent.; the former figure is not derived from his own experience, but from second-hand information; and it is in decided contradiction to the experience of the Tyneside factories, all of them working with open roasters. We shall have to revert to this matter at the close of this Chapter.

In Jones and Walsh's mechanical furnaces a little less sulphuric acid is used than even in blind roasters, just because the mass is much better mixed up and especially because it is always in the state of fine powder, without any lumps and knots; for in the interior of the lumps there is most facility for incompleteness of decomposition; consequently those furnaces turn out sulphate containing only a small fraction of both free acid and common salt.

In the ordinary process such lumps are formed in the pan only with very faulty work; for, under normal conditions, the whole is at first dissolved into a thin mud, which only gradually thickens, but never solidifies; all the more, however, as we shall see, are lumps formed in the roaster.

The proper quantity of acid cannot easily be determined beforehand by mere calculations, owing to the complication of circumstances coming into play; it must therefore be continually checked by testing in the laboratory. We have spoken of this already on p. 12.

In most factories the residue from decomposing the nitrate of soda, the *nitre-cake,* is put into the pans along with the salt, the quantity of sulphuric acid being lessened by the amount of that existing in the nitre-cake as "free acid" (that is, as bisulphate). It is preferable for regular work not to use too much nitre-cake, at most one tenth, better only one twentieth of the salt; otherwise lumpy, poor sulphate is frequently obtained. Nitre-cake is mostly employed in large lumps; but it is much better to grind it, in which case more can be taken and the quality of the finished product will be less injuriously affected.

The requisite quantity of sulphuric acid is frequently run into the pan before the whole of the salt has been shovelled in, by which a better mixture is effected. In any case, afterwards it must be well stirred up with a long-handled rake, till the acid has completely penetrated into the salt and a thin mud has been formed in which the tool does not meet with any resistance; this is called "dissolving the salt." Since herein a very strong evolution of gas takes place, it is well if the working-door has a hole through which the handle of the rake passes; by heaping a little salt against the opening, a pretty tight closing is effected. At this stage the mass has a strong tendency to rise and froth over; consequently a little tallow is now added. The porous common pan-salt dissolves by far the most easily, much less so ground rock-salt, as we have seen on p. 41. When every thing has been "dissolved," the rake is drawn back so that its blade lies close against the door, where it is less exposed to the acid; or it is drawn out altogether after opening the door. In any case the latter is now closed as tightly as possible, either by salt thrown against it, or even by plastering it with clay or lime. Well fitting cast-iron doors, sliding in frames, make this unnecessary, but do not resist

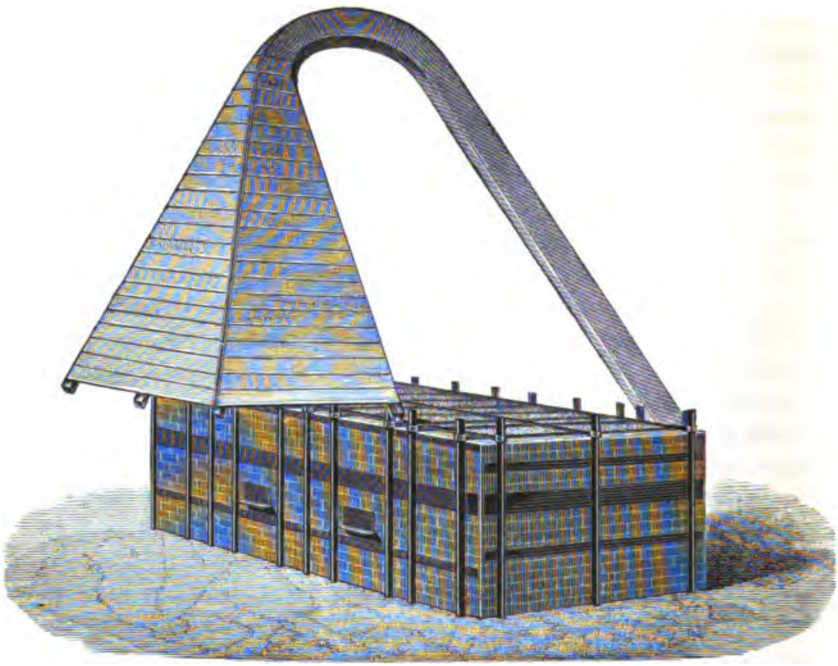
the effect of the acid vapours very long. The door-frames are consequently mostly made of acid-resisting stone or of stoneware, as well as the frame of the damper separating the pan from the furnace. The door itself is made of lead, slate, or even of cast iron; but then it lasts only a short time. A door to be closed with a cross arm and screw-bolt has been already shown in figs. 21 and 22 (p. 53). Most usually the doors are only loosely placed against the frame, and luted by salt belonging to the next charge.

In most cases, during or shortly after raking up the fresh batch, when the evolution of gas is most vehement, but especially on shoving the batch from the pan into the furnace, the escape of a little hydrochloric acid gas into the outer air cannot be prevented. If the condensing-apparatus works properly, it cannot have a great draught; and with the working-door standing open this draught frequently will not suffice for removing all the gas. This also holds good for the working-doors of the roasters, especially on discharging, and even for the damper between the pan and the roaster. In order to avoid a nuisance for the workmen and the neighbourhood, it is advisable to fix *vapour-hoods* over the doors and the damper, made of wood or light cast iron &c., which communicate by means of fireclay pipes with a well-drawing chimney. The quantity of acid vapour escaping therein is mostly so inconsiderable that, after being diluted with the chimney-gas, it is not perceivable. If, however, this source of escape must be avoided by any means, the fireclay pipes may be conducted into a small special condenser; but this will certainly only furnish an extremely weak and practically worthless acid. A hood covering the whole furnace is shown in fig. 80.

Works with very large condensing-space can employ sufficient draught to dispense entirely with hoods.

When the "dissolving" is finished, the mass need only be stirred up once every quarter of an hour; but now the fire must be increased exactly as required for concentrating the mass. Generally the operation in the pan is finished much sooner than the finishing in the roaster; but the last charge must by all means be finished and drawn out of the furnace before the batch is finished in the pan; for otherwise the latter becomes too stiff, cakes to the pan, and cannot be got under at all. The fire must be regulated according to this, and also in such a way that the boiling does not become too tempestuous. On the other hand, the pan should not

Fig. 80.



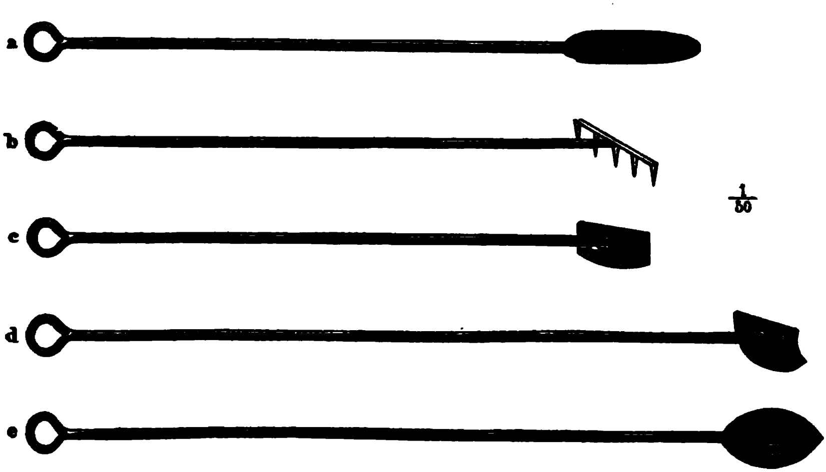
work so slowly that the furnace must wait for it and stand still in the meantime; but this will hardly ever happen if the sulphuric acid be above 124° strong. The whole operation in the pan lasts, in the case of open roasters, one hour, with close roasters from 2 to 2½ hours, on the continent even longer, according to the time the batch stops in the roaster.

A peculiar style of working has been introduced by the Newcastle Chemical Works at Gateshead. Their pans are larger than usual; 18 cwt. of salt are treated in them at a time. Every hour one half of the batch is shoved into the (open) roaster, and another 9 cwt. of salt, together with the corresponding quantity of sulphuric acid, is put into the pan. In this way the pan never becomes empty, except at the end of the week, and suffers much less than usual, so that up to 4000 tons of sulphate can be got out of it before it becomes useless. The work is done in the following way:—On beginning the week, 18 cwt. of salt and acid to corre-

spond are introduced into the pan; when the mass has thickened up to the usual point, half of it (by the judgment of the eye) is shoved over into the furnace; then the sulphuric acid requisite for another 9 cwt. of salt is run in, the mass raked through, 4½ cwt. of salt added, raked through again; the fire is touched up, the last 4½ cwt. of salt are added, raked through, and the batch finished in the usual manner; when it has become stiff, half of it is again shoved into the furnace, and so forth. This style of work has been very successful, and has been introduced by several other large factories.

The batch in the pan is considered finished when the cake cannot be drawn backwards and forwards with ease, but offers considerable resistance owing to the stiffness of the mass. If the setting of the pan is faulty, lumps cake on the hot places of the pan, which are only dispersed with difficulty or not at all. Supposing the contents of the pan to have become stiff, and the roaster-bed to have become empty in the meantime, the damper is raised, the pan-door opened, and the stirring-up rake (fig. 81 *c*) replaced by the tool that serves for moving the batch. For pan-doors opposite to each other (shoving-pans) this is a "shoving-rake," fig. 81 *d*, the profile of which is the same as that of the pan; for pans with doors at right angles to each other (casting-pans) a large hollow "casting-shovel," fig. 81 *e*; and whilst the pan-man moves the contents of

Fig. 81.



the pan into the furnace, the furnace-man from his door at once spreads the charge evenly over the whole furnace-bed.

The *calcining-furnace*, before the charge is moved, should be at a bright-red heat, just as it will be after finishing the previous charge. With blind roasters, at least, the arch should always remain red-hot, so that something can be seen inside. The fresh batch, of course, greatly cools the furnace; and its interior becomes even less visible in consequence of the thick white acid vapours given off. The mass is spread over the furnace-bed with great care,—if the furnace is a double-bedded one, on the top (back) bed; there it is first allowed to dry and is turned over every quarter of an hour, employing partly the paddle or slice, fig. 81 *a*, partly the tooth-rake, fig. 81 *b*. In Lancashire the latter tool is less used than the former; but it contributes very much to an even working-up of the mass, as it prevents the formation of lumps. All the tools are made entirely of wrought iron, the handles $\frac{7}{8}$ or 1 inch thick, and 12 to 15 feet long. The working-parts of the paddles, rakes, &c. being also made of wrought iron, are much lighter than those of the ball-furnaces, whose heat is much greater; but they are quickly spoilt by the acids and must be frequently renewed.

In order to take part of the weight off the men, there are always in front of the working-doors horizontal bars fixed, with a few projections on the top; and hooks hang down from the ceiling, for supporting the back part of the tools.

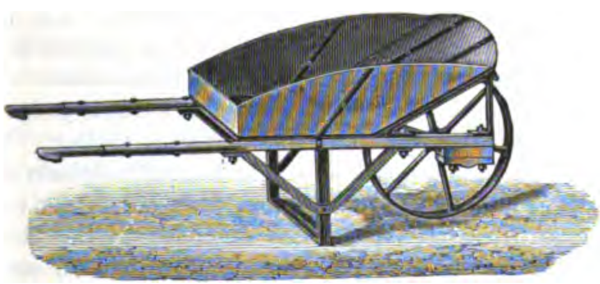
When once lumps have been formed, they can only be broken or crushed with the paddle, which ought to be done in any case. If, however, the batch has become too hot next to the fire-bridge, it there fluxes and cannot be got under with the tools. This is the worst thing which can happen, because such hard lumps are scarcely workable in the ball-furnace; it occurs especially with inexperienced men, and can only be avoided by frequently moving away the stuff next to the firebridge and replacing it by other stuff. Weak sulphate, containing much salt, fluxes much more readily than strong sulphate. All this is much more easily done in open roasters, because the workman can always see what he is doing. Their beds, for an equal make, need only be half as large as those of blind roasters.

Often open furnaces have two or even three beds, sometimes in the shape of terraces, or merely marked by the greater length of the furnace and the arrangement of the working-doors. In this

case the batch coming from the pan is first spread on the back or top bed, and moved forwards to the front bed, which is much hotter, when the previous batch has been drawn out from the latter. Thus the sulphate remains twice or three times as long in the furnace as in single-bedded furnaces, and can be finished at greater leisure. If, for instance, a batch is made in the pan once an hour, this batch remains one hour on the cooler back bed and another hour on the hotter front bed before it is drawn out. In blind roasters the batch is usually at once spread evenly over the whole bed, because here the differences of temperature are not very considerable.

The calcining work is only then finished when no more vapours are given off by the mass, even on turning over, and when it is pretty red-hot; but it ought not to attain the fluxing point at any place. It is now drawn out by means of rakes, fig. 81 *c*, into iron barrows, adapted for tipping over. Fig. 82 shows such a barrow

Fig. 82.



of the shape usual in England. They suffer a good deal from the acid sulphate; and their upper portion must be frequently renewed. At large works there is often a railway running along the furnaces, and four-wheeled trucks run upon this up to the furnace-doors. In front of these there is always a metal plate, because some sulphate is always spilt, which must be kept clean; the front of the furnace below the door must be protected in a similar manner.

In many cases the finished sulphate is not drawn directly into the barrow, because in this operation the escape of acid vapours could not be avoided (which in populous districts might amount to a nuisance), but it is dropped into a cave below or in front of the

furnace, by means of a hole in the furnace-lid usually kept closed; here it can cool down before it is taken out. This arrangement is very rarely found in English works; with the hard-pushed style of work in use in this country it could scarcely be carried out, not merely because it requires much labour to move the sulphate twice instead of once, but especially because the taking-out of the sulphate from the cave would interfere with the furnace-work, and there are not, as is usual on the continent, long intervals between the charges which might be utilized for emptying the cave.

It is just this part of their operations which renders the English alkali-makers the objects of many complaints from their neighbours, if their sulphate-furnaces and warehouses are not at a good distance from public roads, fields, &c. Such complaints are met to some extent if care is taken at once to cover the hot sulphate in the barrows and the storehouse, which, especially in damp weather, emit much vapour with a thin layer of cold sulphate.

The vapour given off by fresh hot sulphate consists mostly of sulphuric acid or anhydride, if the operation has been so conducted as to furnish a strong saltcake, but of hydrochloric acid in the case of weak saltcake (with 3 per cent. $NaCl$ or more). The prickling smell of the latter acid on drawing the batch permits a kind of judgment to be given upon the strength of the saltcake.

Whether the work in the furnace has been good, is judged partly by the appearance of the sulphate, partly by testing. We have described on p. 12 the appearance which good sulphate ought to present: it should be a finely-grained, yellowish-white mass free from lumps. The red colour often exhibited by the lumps does not exactly prove that they contain more iron than the remainder, but merely that the iron, contained in the white sulphate as nearly colourless sulphate, has passed over into red ferric oxide at the higher heat which has caused the lumps to be formed.

The lemon-colour shown by hot sulphate, even such as becomes quite white on cooling, seems after all to come from iron; for it is not shown by the sulphate made in Jones and Walsh's furnace, which contains less iron.

For any irregularities in the outward appearance of the sulphate, such as lumps, fluxings, unequal calcination, &c., the furnace-man (roaster-man) will have to be made responsible,—also if the analysis shows that much free acid is present along with much undecomposed salt. But if a fair average sample shows only either too

much salt or too much acid, this is the fault of the pan-man, and the mixture has then to be changed. Sulphate not containing above ½ per cent. free NaCl and 1 per cent. free acid (calculated as SO_3) may be called very good; even 1 per cent. NaCl and 1½ per cent. free acid are still quite admissible; but these two limits of *fair* sulphate ought not to occur *at the same time*; for if they do, the calcining must have been bad.

The *yield of sulphate* upon the salt decomposed depends on the quality of the salt and the care of the men. In England, from common salt containing from 6 to 8 per cent. of moisture a yield of at least 110 per cent. of sulphate is expected; some calculate 112 per cent.; but the author and other manufacturers known to him have never got this yield for any length of time when *accurately* controlling all the figures, although it may be got occasionally under specially favourable circumstances. With drier salt, of course, a higher yield will be obtained. Pure NaCl would theoretically yield 121·45 per cent. of SO_4Na_2, or salt with 7 per cent. moisture (the other impurities remain in the product) 112·9 per cent. of sulphate, without calculating the free acid. The loss by absorption in the furnace-bed, spilling, &c. can only amount to a small percentage.

The statements of the Belgian Commission, according to which some works only obtained 109, 108, and 102 parts respectively of sulphate from 100 of common salt, either prove an error in the figures (especially for the last case) or an extremely careless style of work. Chandelon reports (Bull. Soc. d'Enc. 1871, p. 323) the result of exact trials with three furnaces at Risle, where from 2700 kilogs. salt, containing 2432 kilogs. NaCl, 3113 kilogs. sulphate (=115 per cent.) were obtained; but it is not stated how much of the 278 kilogs. of the crude salt present otherwise than as NaCl consisted of moisture and how much of other impurities. At a Rhenish works the regular yield is stated at 119 per cent. of the salt, which even with dry salt seems extraordinarily high; 116 to 117 per cent. is generally considered very satisfactory. The yield from the very pure salt of New Stassfurt, which regularly tests 99 per cent. of NaCl, is actually 120 per cent.

We have already seen, in Chapter XV. of Book I., that it has of late become quite usual in England to refer the yield of sulphate direct to the pyrites consumed, so as to be independent of the estimation of the sulphuric acid produced, which certainly can in

no case be called altogether trustworthy. In this way the difference between open and blind roasters as to their consumption of vitriol becomes very clear. In the *best* works on the Tyne (all of them working with *open roasters*) 100 parts of 48-per-cent. pyrites only yield 175 to 178 parts of 97-per-cent. sulphate; 185 may be called the maximum. The true average yield in the best works is, upon 100 parts of sulphur charged into the kilns (not actually burnt), about 380 parts of sulphate—or, assuming that 4 per cent. of sulphur is left in the cinders (=3 per cent. of the sulphur in the pyrites), on 100 parts of sulphur actually burnt, 405 parts of sulphate. In Lancashire, with *blind roasters,* it is asserted that 195 to 200 parts of sulphate are got from 100 pyrites. In most, if not in all, cases this assertion undoubtedly rests either upon self-deception or upon the fact that very poor salt-cake is made; it would answer to 406–417 sulphate upon the sulphur charged, or 433–444 sulphate upon the sulphur actually burnt. In a factory acknowledged to be one of the best-managed in all England, only 430 parts of 97-per-cent. sulphate are obtained upon 100 parts of sulphur actually burnt. This certainly is 6 per cent. more than the above-mentioned yield with open roasters. From the figures of a celebrated French works, fully authenticated to the author, a yield of only 405 parts of sulphate upon 100 parts of sulphur is calculated, and that with *blind* roasters—that is, no more than good English works obtain with *open* roasters; probably there was in this case a larger loss in the manufacture of sulphuric acid.

For the manual labour in decomposing, in England, one man per shift is required for the pan, who also has to wheel the salt and coals and to run the acid; for the roaster usually two men are employed, who have also to wheel away the sulphate. If less than 8 cwt. of salt are decomposed per hour, only one roaster-man is needed. Consequently with blind roasters three men in 12 hours make about 5 batches of 15 cwt. of salt, =4 tons 3 cwt. of sulphate, with open roasters usually 12 charges of 8 to 10, or even 10½ cwt. of salt, =5 tons 6 cwt. to 6 tons 12 cwt., or 6 tons 18½ cwt. of sulphate. They are always paid according to the quantity of sulphate got out. With mechanical furnaces the labour, of course, is much less (p. 105).

The consumption of coals for the pan at a good English works over a long period of time was stated to the author at 15·1 lb., that of coke for the open roaster at 23 lb. per 100 lb. of sulphate. The

author himself has required a good deal less, viz. only 12 lb. of coals and 14·3 lb. of coke, probably because the work was not pushed quite so hard. We cannot give any numerical statements from works where blind roasters are employed and the pans are fired separately. The statements respecting works with blind roasters and the pans fired by the waste heat of these are very contradictory; a German works states its consumption of coals at 34, a French one at 28 to 32, another French one at 46 parts of coals to 100 parts of sulphate. According to the Belgian Report of 1855 (p. 63) the Moustier works averaged 120 kilog. of coals to 300 kilog. salt—that is, 37 parts to 100 parts of sulphate; the Risle works, 133 coals to 351 salt—that is, 35 coals to 100 sulphate.

CHAPTER IV.

THE MANUFACTURE OF SULPHATE BY THE HARGREAVES PROCESS.

Already in a preceding Chapter (p. 29) we have treated of the manufacture of sulphate without the intervention of sulphuric acid, by the direct action of sulphurous acid, air, and steam upon sodium chloride. Patents referring to this process have been taken out, in 1850 by Gossage, in 1853 by Robb, in 1855 by Armbruster and Laist, in 1856 by Rémond, in 1857 by Brooman, in 1858 by Mesdach, in 1863 by Thibierge; also Longmaid's process (1842), itself the revival of a much older process, applies the reaction that comes into play here, certainly in a very different manner from the present. A decisive step was the local separation, first mentioned in Brooman's patent (1857), between the evolution of sulphurous acid from pyrites and its action upon salt. For this reason a patent of Königs and Henderson (June 22nd, 1871), which reverts to a mixture of ferric oxide and salt, without any other novelty of importance, has never had any practical success.

None of the former proposals was successful; even the first-mentioned patent of Brooman's has never been carried out practically; and since the possibility of utilizing that reaction entirely depended upon several accessory circumstances, and especially upon the technical details of the apparatus, the merit of inventors cannot be denied to those two men whose mutual efforts at length made the process successful—especially since they only reached their goal after years of incessant toil and after spending large sums of money. The cost of the many patents taken out by Hargreaves and Robinson in itself represents a small fortune. Most of these patents certainly were only tentative and of no practical use.

Hargreaves and Robinson, of course, do not pretend to have been inventors of the process of making sulphate by the action of sulphurous acid upon common salt in the presence of air and steam; they only claim to have made that process practicable by more than 20 patents. The first of these dates from January 7th, 1870. It only gives an outline of the process; whilst two subsequent patents, of November 8th, 1870, already had all the essential features of the apparatus now in use, but with this great difference, that the gas still rose *upwards* in the cylinders. In their fourth patent, of July 4th, 1871, they introduced the following important improvements:—1st, passing the mixed gases in a *downward* direction through the chlorides, by which a more uniform effect is produced; 2nd, employing cast-iron vessels in lieu of brick chambers; 3rd, combining a series of such vessels in a methodical way, and arranging cast-iron gas-flues, forcing the gas to act gradually upon more and more changed salt, so that the fresh gaseous mixture always comes into contact with nearly finished sulphate, and the almost spent gases with fresh salt, precisely as in the methodical lixiviation of black ash.

Undeniably these improvements have been of decisive importance. The reason why this process, like other pneumatic processes, for instance, that of Deacon for generating chlorine, works much more completely if the gases travel *downwards*, has been treated of in a long paper of Hurter's in Dingl. Journn. ccxxiii. p. 200. He first quotes Hargreaves's own explanation, according to which, in an apparatus of large sectional area, some places are often hotter than others; the hotter places behave towards the colder ones similar to a chimney; if the gaseous current travels upwards, the velocity of the gas in the hotter places is even increased, the temperature rises still more, and thus an originally small difference in temperature ultimately gives rise to considerable diversities. On the other hand, if the current of gas travels downwards, the hotter places allow less gas to pass than the colder ones, because the downwards velocity is lessened by an amount corresponding to the difference of temperature; instead of the chemical activity being increased, it is calmed down; and thus the apparatus always has a tendency to equalize any differences of temperature occurring.

The gaps in this explanation, which at most can only refer to temperatures below 300° C., have been filled up by Hurter by

means of mathematical reasonings. If the temperatures are above 300° C. (which is the case in Hargreaves's apparatus), in Hurter's opinion, everywhere, even if the gases travel upwards, less gas will pass through in the hotter than in the colder places, and consequently, even with the gases carried upwards, the same safety of treatment can be attained as with the gases carried downwards, provided that the velocity of the gas is equal to that which would have been generated by the difference in temperature alone. This condition, however, is very difficult to maintain in practice; and, in particular, it does not exist either in Hargreaves's or in Deacon's process. Consequently the ultimate conclusion is this—that after all a downward current of the gases is always preferable to an upward current, if heat is given off in the reaction. It is true that not every cause of disturbance is avoided in this manner, and pneumatic processes still remain subject to irregularities; for with a large sectional area of the vessels a perfectly equal division of the gas all over the space is extremely difficult, and only when the resistance is a comparatively large one can it be even approximately effected. The principal cause of the irregularity of pneumatic processes is the considerable difference of temperatures, unavoidable in large apparatus; and the efforts of manufacturers must therefore always be directed to filling such apparatus as equally as possible, and heating them just as equally. The latter is best accomplished by applying the above-mentioned principle to the heating-apparatus itself—that is, by introducing the fire-gas from the top, and drawing it away from below.

An equal heating of the whole apparatus was really impossible with the former brick chambers, which required such a strong fire for the heat to penetrate through them that the heating could not be kept sufficiently even. The introduction of cast-iron vessels accordingly marked a great progress. The patent of Hunt (Sept. 8th, 1873), replacing the iron chambers by brick chambers made as gas-tight as possible, was a step backwards, and has not met with any success. A further patent of Hunt's (Sept. 2nd, 1874) prescribes placing the chambers directly above the pyrites-burners, in order to lose as little heat as possible; but the difficulties of building and of charging are greatly increased thereby; and to heat equally is all but impossible in this way; nor does this proposal seem to have been carried out anywhere. No more is this the case with a construction patented by Hargreaves and Robinson them-

selves on Feb. 4th, 1874, viz. a sheet-iron casing between two layers of brickwork.

The most important of H. and R.'s improvements was, of course, that of systematically utilizing the burner-gas, so that it leaves the apparatus at least as free from sulphurous acid as the gas leaving sulphuric-acid chambers. The description following below will make this clearer. Apart from several patents referring to minor matters, that of Oct. 16th, 1872, contains the most explicit descriptions and drawings of Hargreaves's apparatus as it still exists—with one exception, referring to one of the principal difficulties of the process, viz. that of *moulding the salt*. The salt ought to possess a sufficient degree of porosity to make it completely permeable to gases; and it ought also to fill the large chambers in such a way that the gases must traverse it quite uniformly. It cannot possibly be employed in the state of powder, because then the gas would not penetrate through it at all, especially after a crust of sulphate had been formed; it must therefore be formed into lumps. These lumps must be sufficiently consistent to bear the pressure of the superjacent mass, and yet porous enough to be penetrated by the gas to their innermost core and to be completely converted into sulphate. The solution of this problem has only been accomplished during the last few years; and the extension of the process has been greatly retarded by this circumstance. Hargreaves himself proposed (and up to the most recent period it was actually done) to moisten the salt and to dry it very gradually on metal plates, preferably heated by some waste heat; lumps are formed in this way, which are suitably broken up by fluted rollers. The best results are obtained if the salt is very fine previously to being moulded into lumps; and for this reason the very fine "butter salt," or "coal salt," obtained by top heat according to Pohl's process, is most suitable for this purpose—whilst otherwise that salt can be applied to very few uses, owing to its being discoloured by soot. In Hargreaves's apparatus the soot is simply burnt off. Ordinary common salt is usually employed; but ground rock-salt is equally applicable, and is decomposed as completely as common salt, only not quite so quickly. In practice only 10 per cent., or at most 25 per cent. rock-salt is employed along with common salt, both on account of the red colour (from Fe_2O_3) of the English rock-salt and on account of its slower decomposition.

Since the salt dried in this way adheres very firmly to the metal plates or to any other material tried for this purpose, a remedy was found in first covering the plates with a 2- or 3-inch layer of fine dry salt, levelling this, and then putting upon it a 4- or 5-inch layer of moistened salt, in which furrows are made by a shovel, marking off cakes 8 to 12 inches square, in order to assist the escape of steam and to remove the salt more easily. The moistening of the salt has been done for some time past by the exhaust-steam of an engine (for instance, that driving the Roots blower: see below). The salt must necessarily be employed quite dry in the cylinders; otherwise the process goes on irregularly, because any moisture present evaporates in places, condenses in cooler parts of the cylinder, dissolves the salt, and forms dense lumps impermeable to the gas.

On drying by this process, hard, flat cakes are obtained, which must be broken into pieces of about 1½ inch diameter. This, however, causes the formation of much smalls, which must again be subjected to the moistening and drying process; this costs much labour and fuel; and the pieces obtained were nothing like regular enough to permit the filling of the cylinders to be perfectly even. Altogether the drying process took much labour, space, and fuel also, since waste heat was not found sufficient for it. Many proposals have therefore been made to avoid these inconveniences. Thus Hunt patented (June 10th, 1874) the employment of common salt in the shape of regular blocks, perforated with holes at short distances; the holes were to cause the gases to penetrate more thoroughly into the lumps, and also to produce a better draught; half the time of decomposing was expected to be saved in this way. A similar patent was that of Brock (April 23rd, 1875). Neither of them is in practical operation now. Milburn and Jackson on May 26th patented a very complicated moulding-apparatus for the salt. Instead of moulding the salt into blocks at all, M'Dougall (patent of Sept. 4th, 1875) proposed to employ the salt in the loose state, but to keep it in constant motion during the passage of the gas, for which purpose the apparatus patented by him for the burning of pyrites (Vol. I. p. 222) could be employed.

Of greater importance seemed to be the patent of J. C. Stevenson (May 8th, 1875), according to which the moistened salt was moulded at once into pieces of the size and shape of a hen's egg, and dried in an oven exactly like those used for baking ships' biscuits. It

consisted of a long tube, through which an endless chain slowly passed; the moulded damp pieces were put in at one end, and came out dry at the other; the fire-gases travelled through the tube itself and yielded up their heat to the mixture. This was to save manual labour and fuel, to prevent the formation of smalls, and to produce all the pieces of exactly the same size and shape. It was found, however, that the lumps, owing to the strong pressure necessary for moulding, were not sufficiently porous; on the outside a hard crust of sulphate was formed, which surrounded an unchanged core of salt, and extremely retarded the action of the gases upon the same. It was possible to make the decomposition complete, but only in an unreasonably long time, viz. about 50 days, instead of the usual 14 to 20 days.

After all, the drying process is now carried out successfully by the employment of the continuous apparatus first proposed by Mr. Stevenson, but greatly improved by a mechanical contrivance, patented by Mr. Hargreaves. The damp salt is continuously dropped from a hopper onto a row of metal plates connected so as to form an endless chain, which passes through an oven of 5 feet width and 40 to 130 feet length; the heating is done by fire-gases traversing the interior of the oven. Before the end of the plate-chain enters the oven, the salt is pressed down upon it by means of shovels, or mechanically by a roller, and thus converted into a flat cake. At the other end of the oven, where the plate-chain carrying the dry salt comes out, the cake is broken into pieces by hand or by machinery. At the Atlas works (Hargreaves's patent of Feb. 28th, 1877) the salt is moistened by exhaust steam, and, on its passage from the hopper to the endless chain, beaten down by a number of mechanical beaters, imitating shovels in their operation, the beaters being alternately lifted and dropped by canes fixed on a revolving shaft.

This drying process is carried out most perfectly at Messrs. Sullivan and Co.'s works. Here an oven of 5 feet inside diameter and 125 feet length rises in a slope from the ground-level, so that its upper end is above the level of the cylinder-covers. The salt is lifted at the lower end into a hopper by means of an elevator; in the hopper it passes between rollers which crush the larger lumps, and is moistened by the exhaust steam of the small engine driving the whole drying-apparatus. It then falls upon an endless

chain of plates, of the width of the furnace (5 feet), each plate being 12 inches broad. This chain passes through the whole length of the oven, and returns underneath it to the other end. Here the salt is first beaten down by the above-described engine and converted into a layer of 1 to 1¼ inch thickness. Immediately afterwards this layer, whilst moving forward on the plate-chain, is sliced lengthways by revolving circular knives, and crossways by knives moving reciprocally up and down, in a similar but much simpler way than that used in paper-mills for cutting-up the endless paper; the mass is thus divided into small square cakes of about 3½ inches side. These now enter, upon the plate-chain, into the interior of the oven, are slowly carried through, and come out at the other end. For this the plate-chain is continually moved on by a cog-wheel. The cakes of salt coming out at the upper end of the oven fall off as the chain turns downwards, the attendant assisting with a spade pushed behind them. By suitable means (spreading of dry salt, tar, &c.) too strong adhesion of the salt to the plates is counteracted. The cakes, $3\frac{1}{2} \times 3\frac{1}{2} \times 1\frac{1}{4}$ inches, fall upon a grating, where the very limited quantity of smalls which may be formed are separated; they are then ready for charging into the cylinder-covers, situate a little lower down.

The oven is heated by the waste heat of the cylinder-fires, which have previously served for overheating the steam (see below); but, in order to make sure, there is a small fireplace provided over and above that, in which, however, for a weekly production of 130 tons of sulphate only 2 tons of coals at most are consumed. (At South Shields, where the ovens are only 40 feet long, a separate fire is employed for heating them.) In this way the cakes of salt become so dense that they retain their shape in the cylinders, and yet so porous that they are thoroughly converted into sulphate; and as their shape is so regular, the draught in the cylinders also remains regular.

The following drawings will illustrate this description better, though the cutting-apparatus is not included. Fig. 83 is a side elevation; fig. 84, a ground-plan; fig. 85, a sketch of the drying-oven, showing the endless chain and the direction of the fire-gases. The salt is brought from the warehouse in the channel 15 by means of the worm 14, dropped into the hopper 1, and from this gets by means of the rollers *x x* into the channel 2; another worm takes

it to the vertical shaft 4, through which it falls onto the endless

Fig. 83.

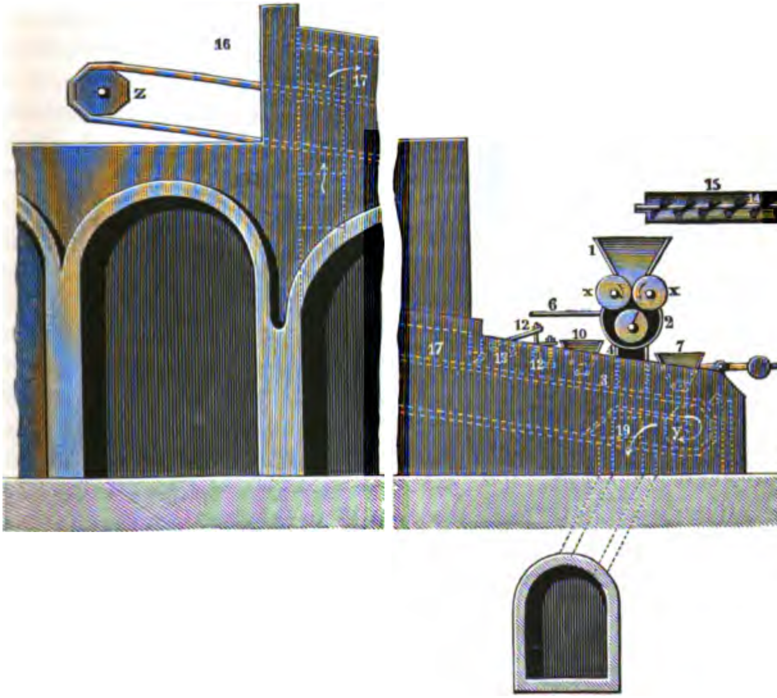


Fig. 84.

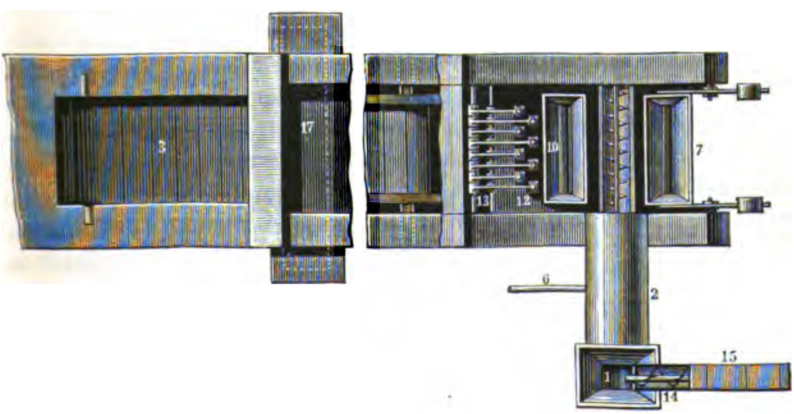
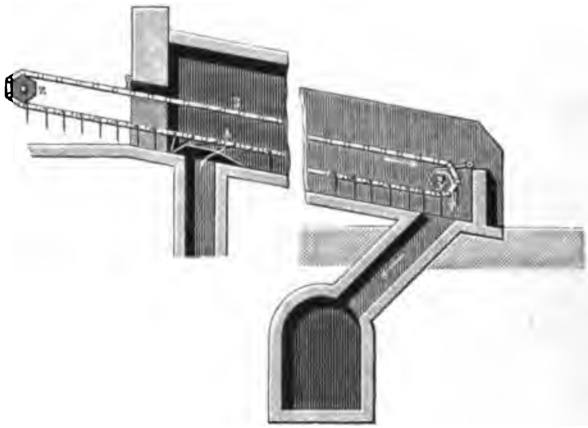


Fig. 85.



carrier 3. The steam-pipe 6, entering the channel 2, serves for moistening the salt. The carrier 3 moves the salt in an upwards slanting direction through the oven 17 to the chamber 16. It consists of two endless chains passing round the drums *y* and *z*; carried by these on swivels, the plates when ascending form a smooth plane, but on returning downwards, when the chains have passed round *z*, hang vertically down. By means of the hoppers 7 and 10, entering into the oven and furnished with fluted feeding-rollers at the bottom, dry salt is sprinkled on the plates before receiving the damp salt, and then on the top of the latter, so as to prevent its either sticking to the plates or to the beaters 12. These consist of horizontal levers turning at one end round a shaft whilst to the other end movable vertical parts are attached, carrying at their lower ends plates slanting in correspondence with the slope of the carrier. Cams fixed on the shaft 13 lift and drop the beaters alternately, and thus compress the salt; the vertical parts of the beaters being movably connected with horizontal ones, the latter are carried along a little way by the compressed salt, till the levers are again lifted by the cams; stirring up the dry covering layer is thus avoided. The carrier now enters the oven, 17, at the upper end of which the hot gases are introduced; these penetrate through the vertically hanging plates into the interior of the carrier, travel along the plates, and at 19 pass into a flue leading to the chimney.

Suitable flaps close the openings for the carrier into and out of the oven.

As a source of sulphurous acid, in Hargreaves's process the burner-gas of pyrites-kilns is always employed, containing besides sulphurous acid the necessary excess of oxygen; here also the aim is to obtain a gas with about 8 volumes per cent. of SO_2, as in making sulphuric acid; but 6 volumes per cent. are allowable. The steam is employed in the superheated state; in the best plants nothing but the exhaust steam of the blowing-engine employed in the process is used. Formerly the steam was always introduced in the gas-pipe leading away from the pyrites-burners. Latterly the attempt has been made to work with single jets underneath the grate of each burner; it was expected that in this way more sulphuric acid would be formed in the kilns themselves, and, moreover, that any too rapid combustion of the pyrites would be moderated. This patent of Hargreaves's was found mpracticable, because the burning was too much interfered with; accordingly the steam is again introduced in the common gas-pipe, or, still better, by a pipe sending branches to the *upper* part of each burner, above the burning pyrites, only the hottest burners being supplied with steam.

The reaction on the salt begins only when it is heated to 400° C., and is the more intense the higher the temperature rises; it is preferable to keep it between 500° and 550° C., lest the effects should be too strong and the material be fluxed. Sometimes pyrometers (for instance, Gauntlett's) are used, with the following rules:—The initial temperature is 400° C.; the proper working temperature for rock-salt is 540°, for common salt 500°, for nitre-salt with 1 per cent. KCl 440° C. At Messrs. Sullivan's, where this process works better than anywhere else, pyrometers have been given up as unreliable.

On leaving the apparatus the gases contain next to no sulphurous acid, but in lieu of it hydrochloric acid, together with an excess of oxygen and especially nitrogen. A certain excess of aqueous vapour should also be present still; at some good works this is fixed at 20 grains H_2O per cubic foot=46 milligrams per litre of the gas. If the evolution of sulphurous acid is not sufficiently strong, and this gas is entirely absorbed before the gaseous mixture reaches the last cylinder, and if steam is absent, the hydrochloric acid, in the presence of an excess of oxygen, splits up, and chlorine and water are

formed; the chlorine, however, is too much diluted to be available for practical purposes.

The normal reaction can be formulated thus (leaving out the elements in excess or not participating in the process) :—

$$SO_2 + O + H_2O + 2\,NaCl = Na_2SO_4 + 2\,HCl.$$

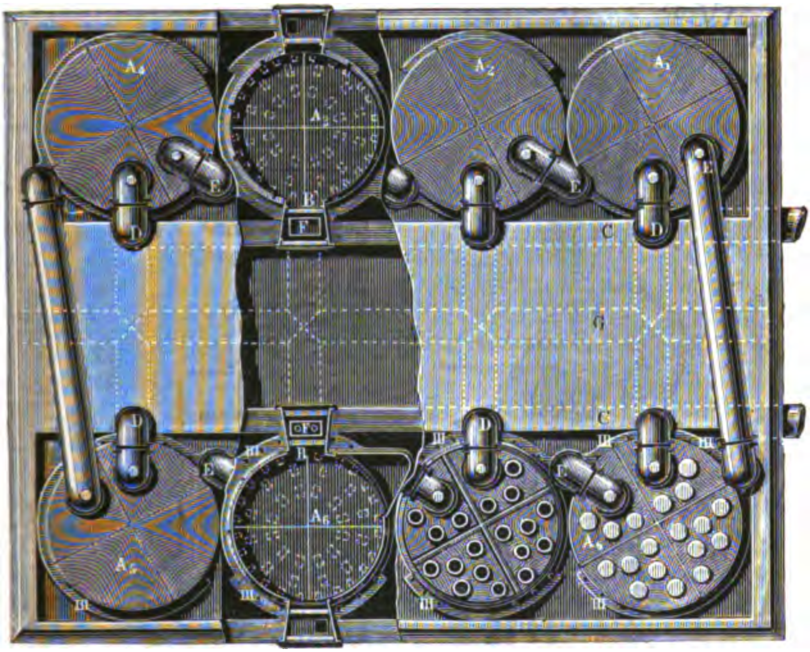
This is evidently a much simpler and more direct process than the usual decomposition of salt by sulphuric acid; and the nitrate of soda is entirely saved, which alone amounts to a saving of about 2*s*. per ton of sulphate.

The following description and diagrams* will explain the present form of Hargreaves's process as it is actually carried out in a number of factories. The salt, prepared in the manner previously described, is placed in cast-iron cylinders, where it remains without further manipulation till converted into sulphate. The minimum number of cylinders is eight; the greater the number, the more regular is the reaction, and the smaller the quantity of fuel required per ton of sulphate manufactured. In fact as many as 20 cylinders are employed. The series of cylinders is so arranged that each in its turn becomes the first, intermediate, and last. The sulphurous acid is first admitted into the cylinder whose contents are most nearly converted into sulphate; and the spent gases pass out from that which was last charged with salt, after passing through a succession of cylinders containing less and less sulphate.

The apparatus shown in figs. 86 and 87 consists of eight cylinders, 15 feet in diameter and 12 feet high, disposed in two rows and marked A_1, A_2, &c. Each of them holds 40 tons of sulphate. They are provided with doors, B, for withdrawing the sulphate. The ground-space between the two rows of cylinders is covered by an arch which is covered with ashes. Along the sides of the two rows and over the abutment of the arch are two iron flues, C, which conduct the sulphurous acid from the burners to the cylinders. The flues are protected from loss of heat by the arch below and a layer of ashes on the outside, the other side being against the heated cylinders. A layer of ashes is also laid over the flues. Ashes form the most efficient non-conducting material readily obtainable, their rate of conduction being only about half that of common bricks;

* Partly taken from a paper by Mr. Hargreaves, read to the Tyne Chemical Society on July 20th, 1875, but essentially modified by more modern data and by the author's own notes and observations.

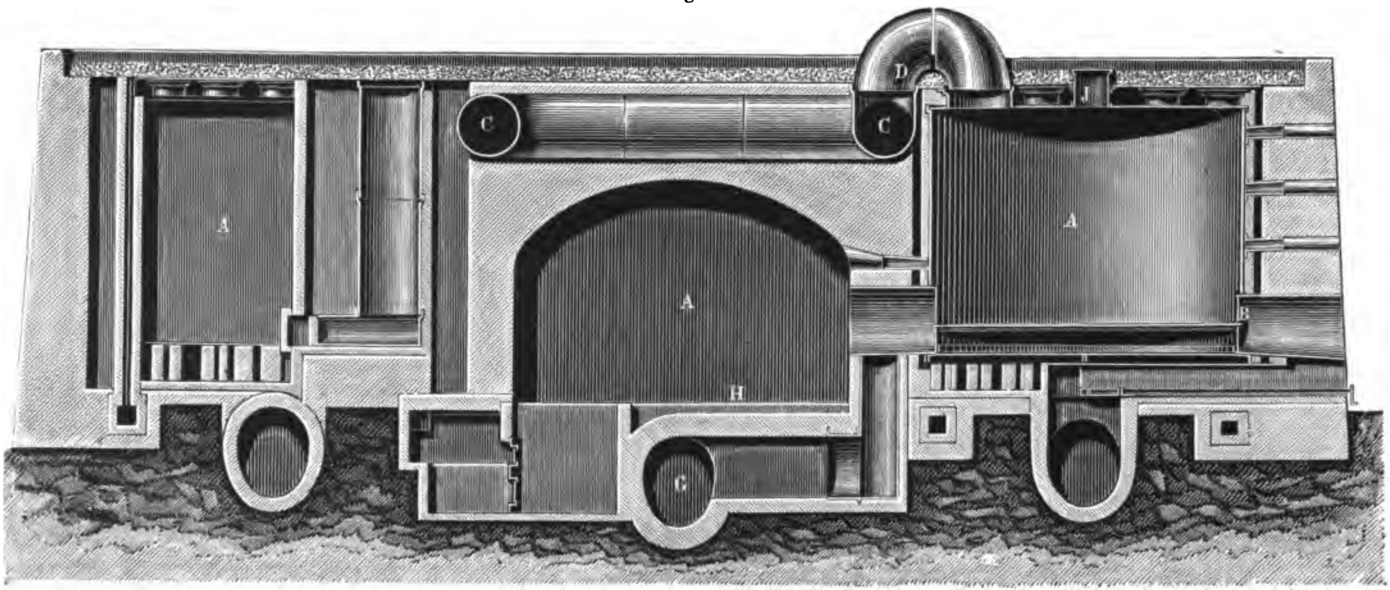
Fig. 86.



besides they cost nothing, and have little weight for a given bulk. Each sulphurous-acid flue, C, has four siphons, D, connecting them with each of the cylinders. The cylinders are connected with each other by the circulating siphons E. When at work the whole of the gas-siphons, except the one connected with the "finishing cylinder" (*i. e.* the cylinder whose contents are most nearly converted into sulphate), are closed, and the SO_2 is allowed to flow into this cylinder alone. Suppose A_3 to be the finishing cylinder and A_2 the exit cylinder, the SO_2-siphon between C and A_3 is open and the circulating siphon between A_3 and A_2 closed, so as to prevent the SO_2 from passing direct to the exit cylinder without going through the whole series. The gas passes in succession through A_3, A_4, A_5, A_6, A_7, A_8, A_1, and A_2, leaving the cylinders by an opening in the bottom of the drawing-doorway, F, whence it passes into the flue G, and is withdrawn by the exhausting-apparatus to be mentioned hereafter.

The salt or sulphate lies upon movable grids, H, which are sup-

Fig. 87.



ported by tripods. These tripods fall readily on striking out small cramps which keep the feet near together, and leave the grids unsupported, when the sulphate is withdrawn. The discharging operation, according to Hargreaves's patent of April 29th, 1875, is to be performed mechanically, by means of an Archimedean screw; but this does not appear to be done in practice as yet. When the sulphate in A_3 is finished, the gas is admitted into A_4 from the SO_2-flue; the circulating siphon between A_4 and A_3 is closed. Whether it is time to cut off the finishing cylinder A_3 or not, is judged from testings of the gas taken out of the siphon leading away from it, for SO_2 and HCl; the change takes place when only 3 per cent. of the SO_2 introduced into this cylinder is found to be absorbed in it. The testings of the gas are performed by aspirating a certain volume from the siphons and titrating it for SO_2 by means of iodine solution, and for HCl by silver nitrate. This test is not strictly correct, since there is always a little sulphuric acid or anhydride in the gas, but is sufficiently exact for practical purposes. The following Table (p. 142) will give an idea of the progress of decomposition. It gives the result of two days' work at a factory possessing a series of 10 cylinders; and it will be noticed from it that the decomposition was practically complete already between the 8th and 9th cylinders.

After withdrawing the sulphate and filling A_3 with salt, the circulating siphon between A_2 and A_3 is opened and A_3 made the exit cylinder. The short pipes J serve as charging-holes to supply the charge of salt. One of these has an annular space around it to admit the products of combustion into the inside of the cylinder, if at any time it is desirable to heat the salt before turning the gases into it; in practice this does not seem to be required. The same space also allows any gases from the inside of the cylinders to pass direct into the chimney-flue, and prevents them from annoying the workmen when withdrawing the charge. In order to avoid this with even greater certainty, the last cylinder, after being finished, is connected for two hours with the exhausting-blower; and thus the HCl, diluted with inert gases, is aspirated into the condensing-apparatus.

The gas from the pyrites-kilns is too concentrated to be allowed to pass directly into the cylinders containing raw salt; for then the action would become so violent as to flux it into a hard cohesive

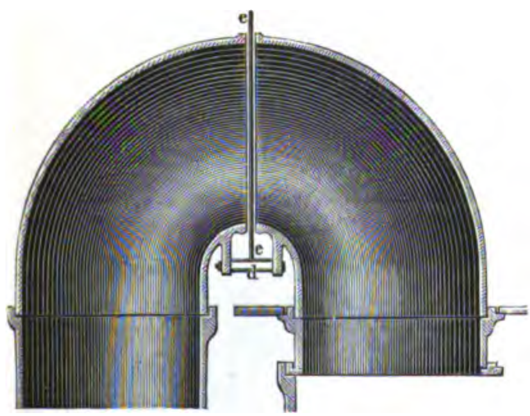
a. Number of the cylinder.	*b.* Found in the volume measured. SO_2.	*c.* Found in the volume measured. HCl.	*d.* Total weight of the acids in the gas.	*e.* Per cent. HCl of the total acids.	*f.* Progress of decomposition.
	grains.	grains.	grains.		
1.	5000	400	5400	7·4	...
2.	4750	1000	5750	17·4	10·0
3.	4250	1500	5750	26·0	8·6
4.	3750	2000	5750	34·8	8·8
5.	2750	3000	5750	52·2	17·4
6.	2000	3500	5500	63·6	11·4
7.	1000	4500	5500	81·8	18·2
8.	500	4500	5000	90·0	8·2
9.	trace	4500	4500	100·0	10·0
10.	trace	3500	3500	100·0	...
1.	3000	200	3200	6·2	...
2.	3250	750	4000	18·7	12·5
3.	2750	1750	4500	38·8	20·1
4.	2000	2250	4250	52·9	14·1
5.	1250	3250	4500	72·2	19·3
6.	750	3750	4500	83·3	11·1
7.	250	4000	4250	94·1	10·8
8.	trace	3500	3500	100·0	5·9
9.	trace	3000	3000	100·0	...
10.	trace	3000	3000	100·0	...

mass. This is avoided by getting up the temperature as soon as possible, and allowing the salt to get covered with a coating of sulphate while at the exit end of the series, where only about one tenth of the original quantity of SO_2 is contained in the gas. The temperature in the cylinders must accordingly be carefully observed, and regulated, in case of need, by admitting more air. For this purpose a 9-inch pipe is sometimes fixed in the centre of each cylinder, open at top and bottom, and reaching down to a few inches from the grids; at the top it is usually closed, and is only opened when there is any danger of fluxing, which, if at all, occurs near the bottom of the cylinder. The covering of sulphate increases in thickness as the cylinder gets nearer the inlet.

The cylinder-connexions are so arranged that, if not properly made, they should themselves call attention to the fact by the annoyance they cause to those who have neglected their duty, besides enabling the manager to see at a glance what was going on. Ordinary valves are impracticable, both on account of the

temperature and the chemical action of the gas; and any SO_2 allowed to leak through to the exit without passing through the whole series is either wholly or partially wasted. To prevent the possibility of this waste, the siphons are divided into two pieces. Fig. 88 shows a longitudinal section, fig. 89 a plan, fig. 90 an elevation of this. The passage of gas is stopped by inserting a plate in the space (*a*) between the two ends of the siphons. The space between the plate and the ends of the siphons is filled up with a mixture of mortar and salt. If this is not properly done, the SO_2 leaks, not into the exit cylinder or an intermediate one, where it might avoid detection, but passes at once into the atmosphere, giving unmistakable evidence that the work is not properly done, and annoying the workman till he looks after it properly. When the passage is to be left open, the plate is replaced by one having

Fig. 88.



an opening equal in area to the siphon. The connexion is made good in the same manner as when the unperforated plate is used. The space between the two halves of the siphon is maintained by the use of the lugs and ferrules, *b*. The opening *c* in the siphon is to allow salt to be charged into the part of the cylinder directly under the siphon.

Fig. 89.

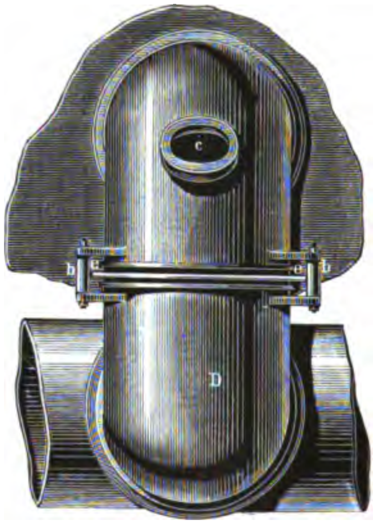
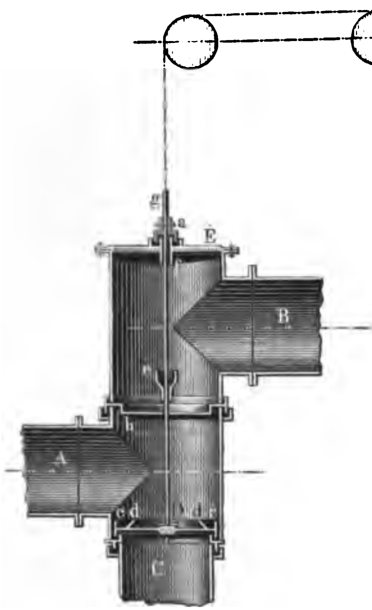


Fig. 90.

Bode has proposed the following modification in Hargreaves's dampers (Dingl. Journ. ccxxv. p. 180). The making-good of the connexions is not easy during an escape of gas; the annoyance of the men and the neighbourhood should also be considered; moreover one opening in the cylinder-covers seems to be preferable to two: Bode's proposal would do away with all this, and would momentarily change the current of the gases. Suppose the pipe A (fig. 91) to lead to the upper cover of the following cylinder

Fig. 91.



(this would be the only opening in the cylinder-cover), the pipe B to come from the bottom of the preceding cylinder, and the pipe C from the SO_2-flue; it will be seen at once that the valve D, filled with sand between the flanges *c* and *d* (*d* can be left out if the whole top is filled with sand), is adapted for opening and shutting, both in the lower position and in the upper one at *d*, all the gasways exactly as required for Hargreaves's cylinders. The lutes are always sand-lutes (which, however, is just an objection to the proposal, as such lutes have not been found to answer in this case); and it can easily be seen how the passage of the valve-rod *g* through

the cover E of the valve-case is closed by a sand-lute, either by the valve *a* or by the cup *e* into which the point *f* enters, and how in this way this proposal might probably be modified so as to become practicable.

It was a difficult problem to heat a series of cylinders 15 feet in diameter and 12 feet high, so as to have all the parts of each cylinder of nearly equal temperature, and to maintain this temperature for fourteen days, without a greater consumption of fuel per ton than takes place when the same materials are kept hot for only an hour or two. Theory, it is true, shows that the heat liberated by the reactions themselves is more than sufficient to keep up the operation and to leave still a large margin for losses by radiation &c., without any consumption of fuel at all. According to Hargreaves's calculations, for each lb. of sulphate there are liberated by the combustion in the pyrites-burners 1426·6, and by the reaction in the cylinders 869·7, altogether 2296·3 British heat-units. The escaping gases, having a temperature of about 300° C., carry away 336·8; the sulphate withdrawn at about 670° C., 316·6 heat-units, leaving an excess of 1642·9 heat-units or 2½ times as much as required, apart from radiation. This latter, certainly, will cause a very great loss of heat till some perfect non-conductor be found, which nobody seriously expects. Still it is possible to make approximate calculations of the unavoidable loss of heat, and of the amount of fuel required for covering this loss. Hargreaves states 15 tons as the quantity of coals necessary for keeping a series of cylinders, producing weekly 100 tons of sulphate, at the proper temperature, provided that the pyrites-burners are so arranged that the heat of the gas is utilized as much as possible. In practice this amount has usually been greatly exceeded, as we shall see below.

The cylinders are surrounded by a casing of brickwork at a distance of 5 inches, and are heated by fireplaces (I). The hot gases pass through a horizontal flue (II), and ascend six narrow vertical flues (III); these flues are only 5 inches square in section, the object being to reduce the heat-absorbing surface where the products of combustion are very hot; the flues, however, are amply large enough to carry away all the products of combustion. The fireplaces are furnished with close-fitting doors, so that when the fires are not needed, both the fireplaces and ash-pits may be secured against admission of air; at the same time the damper (IV) is closed, to stop the draught to the chimney. After leaving the

vertical flues the smoke passes into a space 10 inches deep between the cylinder-cover and an upper covering-plate; it circulates round the charging-holes and over the cylinder-cover; the smoke then passes down the side of the cylinder in the annular space formed by the brick casing, beneath it, and ultimately past the damper to the chimney. Thus the gases where they are hottest are only used indirectly, but afterwards directly for heating the iron cylinders. The cylinder-covers and siphons are covered with about 8 inches of ground rock-salt; if on charging a little of this gets into the cylinders, it does no harm, and it is a further protection against radiation.

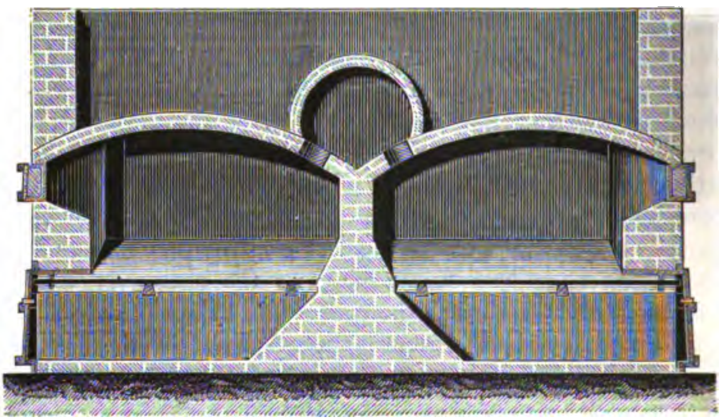
As the heat generated in the process is more than enough to keep up the operation, and the losses of heat are due to radiation and convection from the bounding surfaces of the apparatus, it will be evident that as the apparatus is enlarged, so as to reduce the relative proportion of bounding surface to cubical capacity, the proportion of fuel required per ton of sulphate must decrease, and it is only a question of carrying the principle far enough to do without fuel altogether for keeping up the temperature of the cylinders. This conclusion is confirmed by the experience of working with different sizes of apparatus: one of the first took about 2 tons of fuel per ton of sulphate; a second, larger one, 14 cwt.; this, again, enlarged, 6 cwt.; and the set of eight cylinders in Dublin has worked with 3 cwt., that at South Shields with 2½ cwt.

The Atlas Chemical Company are taking advantage of the fact that the fuel-consumption per ton of sulphate made is reduced, while the production per cylinder is increased where a large number of cylinders are used in a series. They have twenty cylinders arranged in a series and placed back to back, with only one drawing-door and one fireplace, allowing lateral conduction and radiation on one side only. The heat-absorbing surfaces are also reduced by reducing the flue-space.

The pyrites-burners are very much like those used in sulphuric-acid making and placed back to back; but exposure of iron to the direct heating-effect of the burning pyrites is avoided as much as possible. The doorway is without the iron hopper projecting into the inside of the burners. The outside walls are 18 inches thick, preferably using 5-inch fire-brick lining and common bricks for the outer wall. The rate of conduction of common bricks being

less than that of fire-bricks, a saving of heat as well as cost in erection is effected. The back of the arch is thrown lower than the front, and the gas-flue placed in the depression; a wall is raised above the burner-fronts, and the entire space over the burner covered with ashes to a depth of 2 feet or more, to prevent conduction of heat. The door is protected from the heat radiated from the pyrites by a non-conducting lining. Fig. 92 shows the section

Fig. 92.



of a burner in use at Messrs. Boyd and Alexander's. The iron front does not extend more than 2 or 3 inches above the top of the ash-pit, where it is necessary to keep the air under proper control. As will be perceived from the drawing, the surface of iron directly exposed to the heat of the burning pyrites is very small compared with what is usual.

Figs. 93 & 94 show the amount of radiation from iron-fronted burners—one for a burner used in vitriol-making, and the other for one used in Hargreaves's process. The figures show the number of British thermal units radiated per square foot per twenty-four hours at the points marked, measured by a thermoradiometer. In the iron-fronted burners used in Hargreaves's process the loss was 520,090 British thermal units per twenty-four hours from each of the fronts alone, equal to a loss of the heat given off from the combustion of 40 lb. of coal; but as the fuel-efficiency in the sulphate-apparatus is less (certainly not more) than 2000 units per pound

Fig. 93.

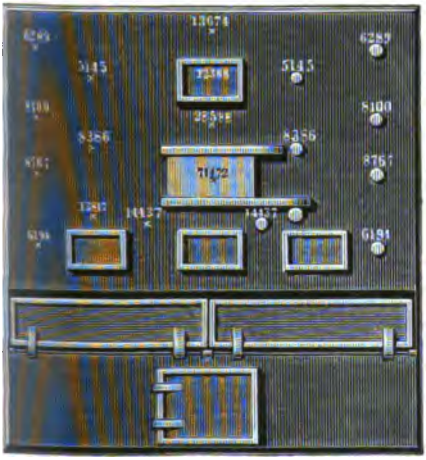
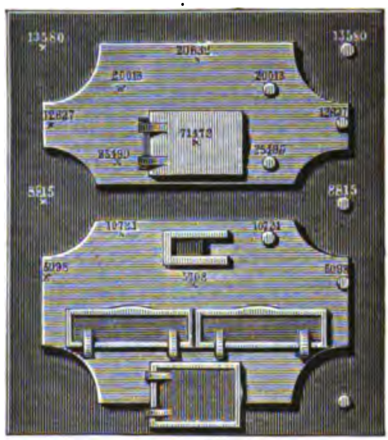


Fig. 94.



of coal, the loss *practically* amounts to 260 lb. of coal per burner per day. As three fourths of this loss is preventable, the *needless* loss amounts to 195 lb., or 2340 lb. per day from twelve burner-fronts; that is, it requires the consumption of 2340 lb. of fuel burnt under the cylinders to replace the avoidable loss of heat sustained in the twelve burner-fronts.

The fuel-efficiency, which of course exhibits large differences according to the nature of the work performed, and which on the whole is by so much the greater the lower the temperature of the material to be heated, in this process is on the average about 14 per cent., varying from 10 per cent. on the finishing cylinders to 20 per cent. on the exit cylinder (where the temperature is lowest). For steam-boilers this term is usually from 50 to 80 per cent., for puddling-furnaces from 3 to 5 per cent.

In order to practise the greatest possible economy of fuel, as much heating as possible must be done upon the materials while they are at a low temperature, so that every advantage may be taken of the temperature-differences. The steam before mixing with the burner-gas, being at only 100° C. (exhaust steam being employed), gives a good temperature-difference to start with; while the products of combustion leaving the cylinders are at about 440° to 470° C., dependent upon the amount of firing going on, and therefore supply an economical source of heat; there is no difficulty in obtaining

steam superheated to 340° C. previous to allowing it to mix with the gas from the burners. The advantage of superheating will be still further evident when the high specific heat of steam is compared with that of gases from the burners. Besides, ordinary steam frequently contains a great proportion of water suspended in it in the shape of minute globules, forming opaque, foggy steam; and this water absorbs heat to convert it into dry steam, rendering some 960 thermal units latent for every pound of condensed water contained in the steam, before raising the temperature of the water; so that practically the elevation of temperature of the mixture by previously superheating the steam is greater than would be shown by calculation if this fact were neglected. The rise of temperature obtained by superheating the steam may be calculated from the formula

$$x = \frac{WST + wst}{WS + ws},$$

in which W signifies the weight of the gas, *w* that of the steam, S the specific heat of the former, *s* that of the latter, T the temperature of the former, *t* that of the latter. It is, of course, absurd to superheat the steam at the expense of the heat of the sulphurous acid gas, as some firms do, by placing the steam-pipes on the top of their pyrites-burners. Another firm prefers superheating the steam by a separate fire, in order to have this process more under control.

Apart from theoretical calculations, an accident has given experimental evidence of the advantages of superheated steam. At Messrs. Boyd and Alexander's the trap for condensed water was placed at some distance from the superheater, instead of close to it; and the water rushing into it when an extra push of steam was laid on, caused a breakage of the cast-iron pipes. This stopped the superheater, and immediately caused an increased consumption of 5 tons of fuel per week in heating the cylinders.

The hydrochloric acid and the excess of other gases are drawn from the cylinder by an aspirating apparatus. The most suitable one is a Root's blower, made by Messrs. Thwaites and Carbutt, of Bradford, modified by replacing the wooden revolving pistons with iron ones, the temperature being too high for the wood to stand without injury, apart from the rapid decay of the wood which would be produced by the corrosive action of the gases. The iron pistons and shell of the blower are not injuriously acted upon by

the gases so long as the temperature is sufficiently high to retain them in a gaseous state; and the blower receives no more damage than it would from drawing the same volume of atmospheric air through it. This temperature is easily retained by placing the machine under cover and putting a layer of non-conducting composition, such as is used for steam-boilers, on the outside shell.

If the parts of the machine subject to friction were allowed to attain the temperature of the gas passing through it, very rapid wear would take place; but this is provided for by making the shafts revolve in brass bushes fixed in a hollow bracket. A current of water is kept flowing slowly through the bracket, so as to keep down the temperature of the brasses; but, from the position of the inlet and outlet holes in the bracket, this water has little cooling effect on the shell. Figs. 95 to 98 show the modifications made to adapt the blower to the process. The shafts pass through holes in the end of the shell, while the revolving pistons are kept in their

Fig. 95.

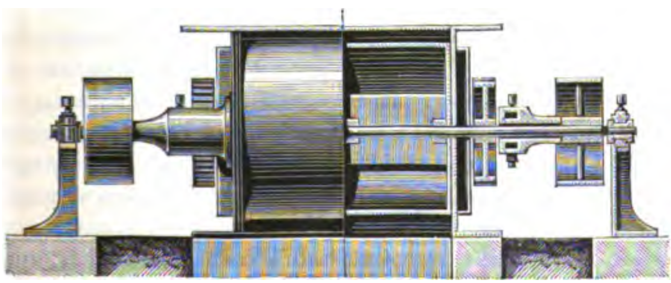
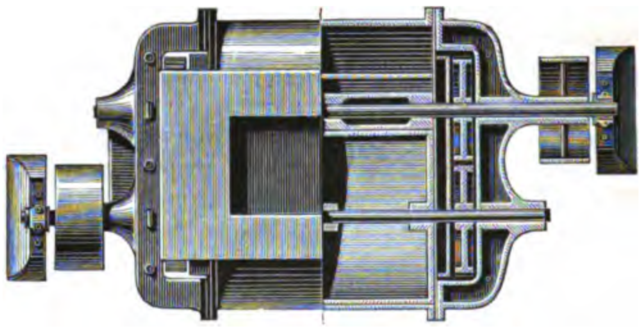


Fig. 96.

Fig. 97.

Fig. 98.



proper relative position by toothed gearing. There is no stuffing-box necessary, as the very small amount of air leaking through is of no practical importance, and there is no tendency of the gases to leak outwards unless great resistance is placed on the exit side of the blower.

The engine driving the blower should be very substantially built and not liable to be stopped for repairs, by which, besides loss of time, the blower cools down, thus permitting condensation of HCl and injuring the blower. The engine should be able to endure without injury the corrosion, hard usage, and negligence which are frequently the fate of engines in chemical works. Mr. Hargreaves highly recommends for this purpose the vertical valveless engine of Mr. James Robertson, of Glasgow. In this engine eccentrics, valve-rods, slide-valve, and connecting rods are dispensed with, and the crank is driven direct from the end of the piston-rod by means of a connecting joint placed on a circular table at the end of the piston-rod; the moving parts of the engine are practically reduced to three pieces, all of which are made exceedingly heavy and strong.

The exhaust steam of the engine driving the blower furnishes the steam needed for mixing with the SO_2; the relative speeds of the blower and engine are such as to send about the proper proportion of steam into the apparatus as the gas is drawn from it. The engine is, in fact, a steam-meter, regulating the supply of steam in proportion to the speed with which the gases are drawn through the apparatus; and as the quantity of steam required for mixing with the gas is in excess of what is needed for driving the engine, the mechanical power for exhausting the gases costs nothing.

A ton of sulphate theoretically requires 2½ cwt.; but about 4 cwt. is used in practice; and from this the fuel needed to supply the apparatus with steam can be calculated. A good boiler, with proper heat-saving appliances, will evaporate 10 cwt. of water per cwt. of fuel; but taking boilers as they are usually found in chemical works, about 7 cwt. would be evaporated; this would give 0·57 cwt. to make steam for a ton of sulphate, and ¾ cwt. would amply cover the steam, loss by condensation, &c.

The amount of fuel consumed at Messrs. Boyd and Alexander's is stated by Mr. Hargreaves as follows, viz.:—

	cwt.
Heating cylinders	4
Preparing salt	3
Steam, say	0·75
Total	7·75

As the steam is taken from a boiler used for other purposes, the weight of fuel can only be calculated; and the fuel for the cylinders includes the use of moist steam, which, when superheated steam was again used, would cause a saving of about 1 cwt. According to more recent information, the fuel consumed is indeed stated at nearly 2 cwt. less than is given in the foregoing Table; but the statements given below make this appear very doubtful. In one factory the author learned the amount of fuel consumed, as follows—viz. total 46 lb. coals to 100 lb. sulphate (bad and good together), of which 12 lb. were consumed for heating the cylinders; here also the drying of the salt and the superheating of the steam are not effected by waste heat, but by separate fires.

It will be seen that Mr. Hargreaves considers the consumption of coals in his process decisive of its value. According to his calculation 3·52 times as much heat is generated by the combustion of the pyrites and the conversion of chloride into sulphate as is carried away by the escaping gases and the sulphate withdrawn; so that 2½ times the amount of those unavoidable losses still remains disposable for radiation of heat; accordingly, with sufficiently improved appliances *no fuel whatever* need be consumed. In the ordinary process of making sulphate the heat is utilized in an extremely imperfect way; the heat generated by the burning of pyrites is nearly altogether dissipated without any utilization what-

ever; that generated by the reaction between salt and sulphuric acid is nothing like sufficient for completing the decomposition; and considerably more heat is required for evaporating and superheating the water mixed with the sulphate. Moreover the chamber-steam must be produced merely in order to be re-condensed in the chambers and to be once more vaporized in the sulphate-furnaces along with the hydrochloric acid. On the whole, Hargreaves calculates that only three or four per cent. of the heat required for all these processes is furnished by the ordinary sulphate process itself. We shall not inquire into the theoretical value of these calculations; but in practice some other circumstances come into play. The great difficulty which exists in Hargreaves's process for utilizing the generated heat is the long time required (as much as three weeks), during which the incessant radiation of even a small quantity of heat must run up to a considerable amount.

Whilst, therefore, the production of sulphate of soda by the old process, including that of the sulphuric acid, in spite of the sources just now mentioned of enormous loss, requires at most from 10 to 12 cwt. of fuel per ton of sulphate, I have trustworthy information that most of the factories working the Hargreaves process require from 8 to 17 cwt., mostly *more* than the old process. The difference, however, is not very considerable, even at present, and will probably be constantly lessened in favour of Hargreaves's process. In the few works where the drying of the salt and the superheating of the steam are done by waste heat, which is undeniably feasible with proper appliances, much less fuel is used than the amount just stated, and certainly no more than with the old process.

It has been found that *the series of cylinders ought invariably to be employed to the full extent of its power*. In some cases irregularities of the process have occurred through leaving one or more of the cylinders empty for a few days: they became too cold; and when it was attempted to reestablish the temperature by strong heating from the outside, the salt was fluxed. In the finishing cylinder, into which the sulphurous acid gas is first admitted, some sodium bisulphate may be formed if the temperature is not high enough, owing to the formation of sulphuric acid in the pyrites-burners themselves; but since bisulphate is decomposed at or below 500° C., its formation should easily be prevented. This is absolutely necessary, since, owing to its easy fusibility, it would

unite the whole contents of the cylinder into a solid lump. If incompletely finished sulphate is discharged from a cylinder, it presents a reddish appearance, owing to ferric oxide, which can only after the complete conversion of NaCl into Na_2SO_4 be transformed into ferric sulphate. In most works such reddish pieces are frequently found, and must be picked out by hand in order to be converted into strong sulphate in ordinary decomposing-pans; otherwise they considerably deteriorate the quality of the sulphate.

A very important question in Hargreaves's process is, to what extent the sulphur of the pyrites is utilized in his apparatus. In practice the operation may not be conducted in such a manner as to leave absolutely no SO_2 in the exit gases; for in this case the hydrochloric acid and the oxygen in excess, in the presence of heated salt and perhaps a little ferric oxide, would yield chlorine. According to the ordinary statements, at most 2 per cent. of all the sulphurous acid is lost with the exit gas; but it would appear as if it had been sometimes overlooked that free sulphuric acid likewise occurs in the exit gas; and thus the real yield may be greatly influenced. We need not wonder why sulphuric acid may escape from the last cylinder in spite of a large excess of common salt present, if we consider that, under favourable circumstances, sodium sulphate may be completely converted into chloride by hydrochloric acid (Hensgen, Deutsch. chem. Ges. Ber. ix. 1671). A statement by G. Davis (mentioned by Mr. Morrison), according to which "the absorption of SO_2" amounts to 99·6 per cent., cannot have taken account of the sulphuric acid, although it is supplemented by the statement that the gas leaving the cylinders contained 0·300 gram HCl, that escaping from the condensers 0·0064 gram HCl, and the condensed acid 0·68 gram SO_3, per litre (at the Runcorn alkali-works). It is not stated over what time the above results extended, nor by what methods they were obtained. The only trustworthy statements are those indicating how much sulphate has been obtained from a given quantity of pyrites, extending over a longer period, which can be compared with the results of the old process. It may be expected that the loss of sulphur in the Hargreaves's direct process will be smaller than in the old process, where the loss caused by the chamber-process, not very considerable by itself, is greatly added to by the more considerable loss of sulphuric acid in decomposing the salt. No very certain data exist upon this point in Hargreaves's process;

at any rate the author could not from the best works obtain any such, but merely the assurance that the yield of sulphate was higher than that of the ordinary process, although even by this at the same works 430 parts of 97-per-cent. sulphate were obtained from 100 parts of sulphur actually burnt. At another works a yield of 182 parts of sulphate from 100 parts of 48-per-cent. pyrites is obtained, corresponding to about 404 parts of sulphate from 100 sulphur really burnt; but here the impure red sulphate, occurring in large quantities, is included, and it would appear that on taking this into account the yield would only amount to 165 parts of 97-per-cent. sulphate from 100 parts of pyrites, or 366 from 100 sulphur actually burnt. Such a low yield would be fatal to the new process; but it is contradicted by the high yield just mentioned, and it is thus proved that there is a great deal in the way in which the work is carried on.

The condensation of hydrochloric acid is facilitated in Hargreaves's process by the steady evolution of the gas; but, on the other hand, the percentage of HCl in a given volume of gas can only be a small one, which makes the condensation more difficult. Suppose the burner-gas to be as rich as in the ordinary process, say at most 8 per cent. SO_2 (and it is certainly not richer); since 4 vols. SO_2 and 2 vols. O yield 8 vols. HCl, the HCl gas will at most amount to 12 per cent. in the exit gas. But the gas from muffle furnaces (blind roasters), according to Dr. Angus Smith, contains from 14·7 to 78·4, on an average 45 per cent. HCl by volume. The gases from Hargreaves's process accordingly can only be compared with that from open roasters; but they have the advantage of a more equal evolution. In this case also no certain data have been given to the world, such as could be called decisive, viz. how much hydrochloric acid is made from a given volume of salt. From his own observations the author can affirm that the condensation is as complete as possible. (At Messrs. Sullivan and Co.'s only 1 grain HCl per cubic foot is left in the gas.) There is also as strong acid made as in the ordinary process, except where the strongest acid is worked for; usually say 26° to 28° Tw. We shall anticipate the Chapter on condensation of hydrochloric acid so far as to state that usually the gas on leaving the blower is admitted into a long stone cistern, from which it issues in three or five strings of fireclay pipes, running alongside, 12 to 16 inches wide and 120 to 180 feet long, cooled by the outer air. The strings of pipes descend somewhat

towards another long cistern, in which the currents of gas are re-united and carried into a stone coke-tower, say 7 feet square and 55 feet high, from the top of which a flue (in one case a wooden one) takes the residual gas downwards into a flue leading to the chimney.

Formerly the *uncertainty of the quality* of the Hargreaves's sulphate was much complained of. Now a much more constant quality is obtained in the best works—at Messrs. Sullivan's 98- to 99-per-cent. stuff is said to be nearly always obtained. But elsewhere, as already mentioned, such good results are not regularly attained, but along with good sulphate much bad stuff is got out, which may principally be owing to the fact that irregularly broken lumps of salt are employed in lieu of the regular cakes made at Messrs. Sullivan's. An important difficulty is this: whilst in managing chambers and ordinary sulphate-furnaces the process can be looked after every hour and mistakes can be corrected, in the direct process nothing is known till the sulphate is discharged, when in a bad case 40 tons at a time may be found all spoiled. The chances of uncertainty in a pneumatic process, like the present one, have been especially pointed out by Hurter (comp. above). Imperfect utilization of the sulphurous acid, incomplete decomposition of the salt, fluxing it into lumps, wrong direction of the gaseous currents, formation of chlorine gas with too little steam, or escape of SO_2 with steam of excessive pressure, are a few of the dangers which are encountered; and their presence is mostly only discovered too late. It is thus not surprising that the management of Hargreaves's process is considered much more difficult than that of the old process; but probably a large number of the difficulties vanish on moulding the salt in such a uniform way as at Messrs. Sullivan's.

At any rate, the Hargreaves sulphate is not, *on the average,* better than the ordinary sulphate; if for once a cylinder full of 98·5-per-cent. is got, another time the strength goes at least as much *below* the average of 97 per cent., which is obtained in the old process with fair work. It should, however, be observed that Hargreaves's sulphate is nearly *free from iron,* at any rate if made exclusively from common salt, and that it is therefore employed by plate-glass works in lieu of refined sulphate or that made in lead pans. All the Lancashire plate glass is made from Hargreaves's sulphate.

The wages in 1878 amounted to 6*s*. 4*d*. per ton of sulphate.

The work is of a much more mechanical character than in the ordinary sulphuric-acid and salt-cake process; and consequently no such experienced and skilled men are needed. All the more care is needed in the management, the incessant testing by gas-analyses &c., and the regular carrying-on of the process.

The plant for Hargreaves's process costs about twice as much as the most substantial plant for vitriol-making and decomposing of an equal quantity of salt. It may be stated at £300 for each ton of pyrites burnt per week, apart from the condensation of hydrochloric acid; whilst the old plant is calculated at £100, or at most £150. On the other hand, it is expected that Hargreaves's cylinders will last much longer and need much less frequent repairs than vitriol-chambers, decomposing-pans, and salt-cake furnaces. This, however, can only be ascertained in the future. At all events, the old iron will ultimately be worth only one fourth part of the value of new iron, whilst old chamber-lead is worth three fourths of that of new lead; and the wooden frame, if strongly built, lasts even longer.

If we are to pronounce finally upon the prospects of Hargreaves's process, we shall not find this quite an easy task. A few years ago English alkali-makers had such a high opinion of that process that no new vitriol-chambers were built, and the question was discussed whether it was more worth while first to work down the existing chambers, or to defray the cost of the new plant at once. But afterwards a less sanguine opinion gained ground; and when Jones and Walsh's mechanical sulphate-furnace opened out the prospect of greatly simplifying and cheapening the decomposing process, it seemed as if Hargreaves's process would again recede into the background. Since the success of the mechanical decomposing furnaces has turned out at present to be limited, the question is exactly where it was before.

The *advantages* offered by Hargreaves's process are as follows, viz.:—a very large saving in ground-space; the saving of nitre; the manufacture of very strong sulphate almost free from iron (if every thing goes right); emancipation from the pan-men, who are difficult to get and worse to keep right, and whose spite or carelessness may cause enormous damage by the breakage of pans; probably also a higher yield, and smaller loss of sulphur (this point is very much disputed); a steady evolution and consequently comparatively easy condensation of hydrochloric acid, in spite of its being excessively diluted with nitrogen and oxygen;

comparative freedom from nuisance by escaping gas, since the lead-chambers and decomposing-pans and furnaces, always wanting repairs and difficult to keep gas-tight, are replaced by tight cast-iron cylinders, into which gas is aspirated and thus cannot leak out—though on withdrawing the sulphate and from the dampers in the siphons losses of gas used formerly to occur, which have now been done away with, as we have seen above; lastly, it is *expected* that the apparatus will need very few repairs.

The *drawbacks* of the new process are as follows, viz.:—much higher prime cost of plant than for the old process (although on a smaller ground-space); possibly larger cost of maintenance, if any of the cast-iron cylinders should wear out (upon this point, as well as upon the cost of wear and tear generally, no decisive experience is as yet in existence); greater consumption of coals, at least in the majority of works, notwithstanding Hargreaves's assurances; but by far the greatest drawback in most cases is the above-mentioned inequality of the process, which proceeded most of all from the salt not being prepared in a thoroughly satisfactory way, exacting an extremely difficult supervision and causing frequent troubles. We have seen above that, at least in one or two places, the difficulties of a proper preparation of the salt have been completely overcome; and here the process certainly works in a most satisfactory way; it is preferred to the old process, which is only retained in order to use up the existing apparatus. Where, however, the salt is still prepared in a rougher way, especially where it is broken up by hand, the above-mentioned irregularity in the quality of the sulphate at once sets in; and there the value of the process is regarded as very doubtful. For a smaller make than at least 15 tons per diem, the process does not seem to be adapted.

Up to the present the following plants, according to Hargreaves, have been erected:—by the Atlas Chemical Works at Widnes; by Messrs. Sullivan and Co. in the same place; by Messrs. Golding, Davis and Co., also at Widnes; by Messrs. Wigg, Steele, and Co. and by the Runcorn Alkali Company at Runcorn; by the Jarrow Chemical Company at South Shields; and by Messrs. Boyd and Alexander at Dublin. Nominally six of these works (apart from Messrs. Golding, Davis, and Co.'s) were to furnish the considerable quantity of 70,000 tons per annum; but only about half of this quantity is actually got out.

The latest alterations of the Hargreaves plant, as carried out at

Messrs. Golding, Davis, and Co.'s, are as follows:—There are twelve cylinders 14 feet deep, instead of 12 feet like all the others. The flues above the covers and underneath the bottoms are omitted; the covers are simple, but covered with a double layer of ashes for preventing radiation. The exit gases are not taken away at the bottom of the discharging-hole, but from the circulating siphon, rising upwards, and thence by a loose siphon into a square flue running over the cylinders.

A patent of Hutchinson's (dated Jan. 1st, 1876, and already mentioned on p. 30) aims at the production of alkaline sulphates from their chlorides, by a process similar to Hargreaves and Robinson's, viz. by treating salt with a heated mixture of sulphurous acid, air, and steam, but carried out in a totally different way, viz. by dropping the chlorides as a spray into a space filled with the highly heated vapours. This does not look very promising; we cannot learn whether it has ever been practically tried.

Another variation of Hargreaves's process has been patented by Storr, Best, and Morris, on April 10, 1877. The gas of the pyrites-burners is to be admitted into the lower portion of a coke-tower, in which a solution of potassium or sodium chloride runs down; at the bottom a solution of snlphates flows out; at the top hydrochloric acid gas leaves the tower. The success here promised does not appear probable.

CHAPTER V.

COSTS, PURIFICATION, AND APPLICATION OF SULPHATE.

Costs.

Chandelon (Monit. Scient. 1864, p. 49) gives the following cost-accounts of two English (Widnes) and two Belgian works, each for 1000 kilog. of sulphate.

A. *English works.*

			francs.
531·5 kilog.	sulphur at 46 per cent. sulphur, @ 43·10 francs per ton		22·91
30·33 „	nitrate of soda, @ 344·82 francs per ton........................		10·47
875·5 „	salt, @ 8·93 francs per ton ...		7·82
575 „	coals, @ 5 francs per ton		2·87
Labour	....		8·0
			52·07
Repairs	....	4·93	
General expenses	....	6·16	
			11·09
			63·16

B. *English works.*

			francs.
582 kilog. pyrites at 46 per cent. sulphur, @ 43·10 francs			25·08
33·5 „ nitrate of soda, @ 344·82 francs			10·47*
875·5 „ salt, @ 8·93 francs			7·82
200 „ coke, @ 13·95 francs			2·71
325 „ coals, @ 4·93 francs			1·60
Wages			8
			55·68
Repairs	4·93		
General expenses	6·57		
			11·50
			67·18

C. *Belgian works.*

			francs.
894·5 kilog. pyrites smalls, @ 27·80 francs			24·87
Clay for making balls			·80
33·5 kilog. nitrate of soda, @ 412·50 francs			13·81
44·5 „ sulphuric acid, @ 65 francs			2·89
846 „ salt, @ 32·50 francs			27·50
1318 „ coals, @ 9·65 francs			12·72
Wages			15·25
Lighting			·37
			98·21
Repairs	6·02		
General expenses	5·92		
			11·94
			110·15
Deduct value of the nitre-cake			3·89
			106·26

* This is an error; it should be 11·55.

D. *Belgian works.*

			francs.
912	kilog.	pyrites at 36 per cent. sulphur, @ 35 francs	31·92
29	„	nitrate of soda, @ 345·58 francs	10·02
900	„	salt, @ 35 francs	31·50
1153	„	coals, @ 8·70 francs	10·02
Wages			12·90
Lighting			·35
			96·71

(Add to this repairs and general expenses.)

Chandelon adds the following remarks. It appears from the cost-accounts that the English works consume less pyrites, coals, and wages than the Belgian works. For 1000 kilog. of sulphate the English works only consume 256 kilog. of sulphur, against 328 kilog. in the Belgian works—partly because they burn off the pyrites more completely, partly because they employ less sulphuric acid in decomposing the salt (we shall see below that this is a mistake). The smaller consumption of fuel and the smaller amount of wages on the whole, whilst each man earns much more in England than in Belgium, are accounted for by the large scale of operating: in Belgium each furnace decomposes 1500 to 1800 kilog. salt daily, in Lancashire 11,000 to 12,000 (this is greatly exaggerated). In Belgium the pan is heated by the waste fire of the roaster; in England each has its own fire, which permits of much quicker work.

To these remarks we must add the following observations. Chandelon's figures, if they were trustworthy, would prove that the supposed saving of coal when the pan is heated by the waste fire of the roaster is quite illusory; for as this compels a much slower style of working than with separate fires, twice as much fuel is ultimately consumed in the cases quoted, to say nothing of a similar increase of expenditure in wages and higher cost of plant. On the contrary, E. Kopp (Monit. Scient. 1866, p. 611) remarks that in France, similar to Belgium, a slow style of working is preferable, because wages are cheaper and coals dearer than in England! (It will be seen from the statements made on p. 127, that in France certainly more fuel is consumed than in England, probably not

owing to, but in spite of, the slower work; only with work pushed on as fast as possible is there undoubtedly more coal used in England.)

It cannot be said that the English product is inferior; and as to the condensation of hydrochloric acid, undoubtedly the most difficult problem with quick work, experience has shown that complete condensation is also attainable with the latter, if only suitable appliances are provided.

We have further to remark with reference to Chandelon's figures, that they state the consumption of nitre in the two English works at 12½ per cent. on the sulphur—that is, three times as much as is used now-a-days, when the nitrous gas is recovered, which was not the case at that time. The second Belgian works (for the first the percentage of the pyrites is not stated) only requires 9 per cent. nitre on the sulphur—but, to all appearance, just for this reason, because the sulphur was very insufficiently burnt off (down to 6 or 12 per cent., according to Chandelon), and because, moreover, nitre was too much economized; from this no doubt arises the bad yield of vitriol, and the large consumption of sulphur for the same quantity of sulphate. Here also is economy in the wrong place. No doubt it is very instructive to analyze such calculations; but this should always be done with discrimination and with the guidance of practical experience. From this the author makes bold to assert that Chandelon's accounts of English costs are too rose-coloured, at least as to the consumption of pyrites on the one hand, and to the yield of sulphate (114 per cent. of the salt) on the other. It is simply impossible to make 1000 parts of sulphate with only 244 parts of sulphur in the pyrites *charged*, seeing that the sulphate itself contains 225 parts of sulphur; and certainly, at that period, even 266 parts of sulphur did not suffice, since even in our days, with greatly improved appliances and increased yields in vitriol-making, according to all the author's experience and information, very rarely below, but nearly always above 266 parts of sulphur in the pyrites bought or charged (different from the sulphur actually burnt) is required.

E. Kopp (*loc. cit.*) quotes the following cost-account of sulphate in England, for 1866, which cannot be directly compared with the foregoing, because it does not start immediately from pyrites, but from sulphuric acid. It refers to an open roaster.

For 100 kilog. sulphate there are required :—

		francs.
88 kilog. salt, @ 10 francs per ton		0·88
88 „ sulphuric acid at 60° Baumé, @ 60 francs per ton		5·28
20 „ coke, @ 14 francs per ton		0·28
30 „ coals, @ 7 francs per ton		0·21
Wages		0·40
		7·05
General expenses	0·35	
Repairs	0·40	
		0·75
		7·80

Here also the yield on the salt is assumed too high, but the cost of sulphuric acid is assumed quite disproportionately high, as if it were not made at the works, but bought in carboys; this explains the extraordinarily high price, in England, of the sulphate.

The following is a statement, from the result of a normal year in the author's own experience, of the cost for sulphate made with open roasters: 1000 kilog. of sulphate required

	£	s.	d.
913 kilog. salt with 5 per cent. moisture, @ 14*s*.	0	12	9·4
959 „ sulphuric acid at 144° Tw., @ 28*s*.*	1	6	10·2
160 „ coals, @ 5*s*.	0	0	9·6
195 „ coke, @ 14*s*.	0	2	8·8
Wages	0	4	3
Repairs (exclusive of broken pans)	0	1	3
Average cost of broken pans	0	0	5
	£2	9	1

In order to make this calculation comparable with those of Chandelon, we will state the requisite quantities &c., starting directly from pyrites, viz.:—

* This is cost to the maker, with pyrites much dearer than at present.

591 kilog. pyrites at 48 per cent. sulphur.
11·3 „ nitrate of soda.
913 kilog. salt.
370 „ coals and 195 coke.
Wages, *7s. 3¼d.*
Repairs (inclusive of the renewal of chambers), *2s. 7·2d.*

In none of these cost-accounts is the value of the hydrochloric acid, obtained as a by-product, reckoned.

At several factories on the Tyne it is asserted that they only require 540 parts of pyrites for 1000 parts of 97-per-cent. sulphate; at others in Lancashire, the amount stated is only 513 parts of pyrites (details on p. 126); but since, as a rule, statements of yields are very unreliable, and every manager represents his results in the most flattering light, such statements cannot be implicitly accepted, and the author has preferred to base his account of the costs upon much less favourable data. Theoretically 1000 parts of 97-per-cent. sulphate would only require 218 parts of sulphur or 455 parts of 48-per-cent. pyrites; the loss of about 20 per cent. of sulphur is to be accounted for partly by the residual sulphur in the burnt ore, partly (but to a very slight extent) by a loss of gas in the chamber process, partly (to a much greater extent) by the excess of sulphuric acid employed in decomposing the salt.

Purification of Sulphate of Soda. Manufacture of Glauber's Salt.

This operation is only practised upon a very small fraction of all the sulphate manufactured. In the first place, of course, all sulphate of soda required for pharmaceutical purposes must be purified, for which purpose it is also brought into the state of crystals or "Glauber's salt." Otherwise the latter are very little used, since their large percentage of water makes their carriage expensive and prevents their employment for many purposes without previous drying, for instance for glass-making.

For pharmaceutical purposes Glauber's salt, which is usually supplied already in the crystallized state, is purified by dissolving in one third of its weight of tepid water (say at 33° C.), filtering, and cooling. In case of need a few soda crystals are added in order to saturate any free acid present and to precipitate any iron.

Sometimes the sulphate must be purified on a larger scale for glass-making, if it is required all but entirely free from iron—for instance, for plate glass. Most of the sulphate employed for this purpose is not made by purifying crude sulphate (which is an expensive process), but by direct preparation of sulphate comparatively free from iron in lead pans; this sulphate has recently been driven out of the market in many places by that which is made by the Hargreaves process. At some places, however, it may happen that pure sulphate must be made from the crude product by dissolving, precipitating the impurities, settling, and boiling down. For plate-glass-making especially, it is important to remove as much of the ferric oxide as possible, because it is converted by the coal contained in the glass-mixture into ferrous oxide (silicate), the green colour of which is much more visible in the thick plate glass, than in sheet glass. Crude sulphate usually contains from 0·1 to 0·3 per cent. iron, sometimes more, which by refining can be brought down to 0·006 per cent.

The apparatus and process employed at the St.-Gobain plate-glass works near Stolberg have been described by Jaeckel (Dingl. Journ. clxi. p. 109). There is an iron tank about 4½ feet long, 4 feet wide, and 3 feet high, with water- and steam-pipes. The water is heated; and then the sulphate is put in in suspended sieves. When the liquid has attained a strength of 57° Tw., which for each tank takes about 8 cwt. of sulphate, the sieve is taken out, and about 28 lb. of lime, slaked to a thick mud, are added and well stirred up; after four hours the clear solution is drawn off by means of lead siphons from the brown mud, standing about 5 inches high. The mud is washed with hot water, and the washings employed for dissolving fresh sulphate. The strong liquor is boiled down in pans 8 feet long, 5 feet wide, and 1½ foot high; and the small crystals formed in boiling are fished out and drained. Each pan furnishes in each operation (12 hours) about 10 cwt. of sulphate. The latter is then dried in reverberatory furnaces, which are charged every four hours, and each time furnish 5 cwt. of dry sulphate. The whole plant (which makes the impression of an unsuitable multiplication of small apparatus in lieu of employing a few large ones) cost £405. The average loss on the refining is 7 per cent. The costs were as follows:—

	£	s.	d.
1612½ kilog. sulphate, @ 15*s*. per 100 kil.	12	1	10
50 „ lime	0	0	5
Wages (10 men)	0	19	3
Coals, 28 "Scheffel"	0	15	3
General expenses and repairs	1	6	9
Yield: 1500 kilog. of refined sulphate =	£15	3	6

The author has himself refined several hundreds of tons of sulphate for plate-glass-making in a similar manner, employing exactly the same apparatus as for making "refined alkali" from common soda-ash; the process also is so similar to that of refining alkali, that its special description may in this place be omitted. We will only mention that, after dissolving, the solution was boiled with exactly sufficient lime and a very little bleaching-powder, in order to obtain a perfectly neutral, limpid solution quite free from iron, which, after complete settling, was boiled down in a pan by an open coke fire; the salt was dried in an open furnace, and ground.

Instead of separating the sulphate by evaporation, it may be crystallized by cooling, and from the crystallized Glauber's salt with 10 molecules H_2O the anhydrous sulphate prepared by Pechiney's process (German Patent, No. 1842, Jan. 12th, 1878). The Glauber's salt is heated in a pan furnished with an agitator, by means of steam, to a temperature of 40° or 50° C. When it has been melted in its water of crystallization, common salt or magnesium sulphate, or a mixture of both, is added, whereupon the anhydrous sulphate is separated and can be obtained by filtration or by a centrifugal machine. With 16 to 20 parts of common salt to 100 parts of Glauber's salt, 90 per cent. of the latter can be precipitated; with 45 parts of mixed salts, as they are obtained at salt-works (*i. e.* $45\,NaCl + 55\,MgSO_4$), to 100 parts of Glauber's salt, the latter is completely precipitated.

Sometimes the sulphate is not to be sold in the anhydrous, but in the *crystallized* state, as *Glauber's salt*. The quantity of the latter made is not very great since its use has been restricted principally to medicinal purposes, whilst formerly it served very largely for adulterating soda crystals and Epsom salts. For this purpose the sulphate is dissolved just as for making ordinary refined sulphate; but the settled warm solution is not boiled down, but filtered

through a linen cloth and run into coolers. If the latter are large and shallow (say 1 to 1½ inches deep), and if the liquor is protected against shaking, it crystallizes in long, thick, transparent prisms, very similar to soda crystals; the mother-liquor is run off by opening a plug-hole in the bottom of the cooler; the crystals are taken out by means of a spade or, in case of need, of a crow-bar, spread on a deal bench till they are superficially dried, and packed into casks before the drying has proceeded to incipient efflorescence. By adding 12 parts of soda-ash to 100 parts of sulphate the crystals are obtained a good deal larger, firmer, and more like soda; this is done expressly for the purpose of selling the product as "best Scotch soda" (Swindells, Chem. News, xvi. p. 227)!

If, however, the crystals are to be obtained as small as possible, the settled liquor is run into deeper coolers and, as soon as the temperature sinks below 33° C., it is slowly stirred with a wooden paddle till it has cooled down completely. Thus the crystallization is disturbed, and instead of the large prisms, small needles are formed which closely resemble Epsom salts and formerly actually were sold by this name. They were altogether only made for adulterating-purposes; but with the present low price of real Epsom salts this would not pay. Such mock Epsom salts can be instantly distinguished from the real article by a solution of soda, which gives a precipitate with the latter, but not with the adulterated article unless it contains some real Epsom salts.

The coolers may be, on a small scale earthenware dishes, on a larger one wooden tubs (difficult to keep tight), wooden cisterns lined with lead, also cast-iron or wrought-iron vessels; but these, before use and every time they stand empty, must be scoured bright with a brick or with pumice; and in spite of this, rust-spots upon the crystals adhering to the sides cannot usually be avoided. This can be done by painting the well scoured and dried surface with a double coat, say, of iron minium (ferric oxide and clay) and boiled linseed oil, adding some drying-preparation. The paint must be renewed from time to time.

Applications of Sulphate.

Probably a larger quantity of sulphate of soda is produced than of any other chemical product, except the metals and sulphuric acid itself; but only a small portion is consumed otherwise than

as an intermediate product in alkali-making. Most of the sulphate otherwise employed is used in glass-making, the purer article for plate glass and white bottles, the crude article for sheet glass and green bottles. Other applications are :—for making ultramarine; for Glauber's salt; for impregnating seeds as a protection against rust (Wagner's Jahresb. 1856, p. 189); for decomposing the calcium chloride in the mother-liquors of saltpetre works; for decomposing calcium acetate in making sodium acetate; for manufacturing the hydrochlorite, hyposulphite, and several other salts of sodium from the corresponding calcium salts.

The crystallized salt is employed in medicine, especially for veterinary purposes, and in chemical laboratories for cold-producing mixtures.

CHAPTER VI.

GENERAL NOTES ON HYDROCHLORIC ACID.

Historical.

The ancients were already acquainted with the cementation of argentiferous gold by heating it with common salt and copperas or alum, in which case hydrochloric acid is set free and comes into action. To the Arabian alchemists aqua regia was well known; but pure aqueous hydrochloric acid is first mentioned by Basilius Valentinus in the 15th century. At the end of the 16th century Libavius mentions its evolution by heating with clay; Glauber still (1648) calls it the dearest of all acids and the most difficult to prepare! He kept secret its preparation from salt and oil of vitriol, discovered by himself. He also knew the hydrochloric acid gas; but Priestley first collected this gas over mercury, and described, in 1772, its properties (details in Kopp's 'Geschichte der Chemie,' iii. p. 346).

Chemical Properties of Hydrochloric Acid (Muriatic Acid, HCl).

Hydrochloric acid is sometimes found in nature in the free state or in aqueous solution—for instance in volcanic exhalations, springs and brooks, and in the water of some rivers along with free sulphuric acid (Vol. I. p. 16). In the animal body hydrochloric acid is mostly present, because the stomachic glands secrete it, and thus the gastric juice contains it, at least at times. Thus the gastric juice of the dog on the average contains about 3 per cent. HCl. In the salivary glands of *Dolium galea*, also, 0·4 per cent. HCl is found along with free sulphuric acid. Hydrochloric acid is formed synthetically from its elements if they are mixed in equal volumes and exposed to the daylight; upon this action

Bunsen and Roscoe's method for measuring the chemical action of light-rays is founded. In the direct light of the sun the two gases unite with an explosion; also by heating and by the action of the electric spark (the latter even when much diluted by air), but not by the action of platinum sponge.

Hydrochloric acid is formed besides by the action of chlorine on all compounds of hydrogen (except hydrofluoric acid), and especially on organic substances under various conditions; also by the action of hydrogen, and especially of hydrogen compounds, on many chlorides. The only way of preparing it in practice is by the action of sulphuric acid upon common salt and, in Hargreaves's process that of sulphurous acid, along with atmospheric air and steam upon the same; the *preparation of that acid from chlorides containing water of crystallization, especially those of calcium and magnesium,* has not yet been technically successful. It appears that Pelouze first proposed this process (Compt. Rend. lii. p. 1267): he found that calcium chloride, mixed with sand in order to prevent fusion, was completely decomposed at a red heat with evolution of large quantities of HCl. This suggestion has recently been taken up again by Solvay, in order to utilize the calcium chloride obtained as a by-product in making soda by the ammonia-process, and in many other technical processes (English patents of Jan. 9th and 12th, 1877). He prescribes to evaporate the solution of calcium or magnesium chloride almost to dryness, to mould the residue with sand or clay into balls or the like, to put these into iron or brick towers heated from the outside, and to conduct a current of superheated steam through the same; HCl escapes, and can be condensed in the usual manner, or else it is allowed to act upon the silicates or aluminates obtained before: thus, on the one hand, $CaCl_2$ or $MgCl_2$ is obtained back again, and, on the other hand, finely precipitated silica or alumina. The silicates or aluminates may also be employed directly in the manufacture of soda by the ammonia process for decomposing the solution of sal-ammoniac (comp. Book III. Chapter XVI.). Solvay founds this process on an observation which he believes he has made, that in the presence of calcium chloride and steam, and at a very high temperature, alumina behaves like an acid and liberates HCl from $CaCl_2$ or $MgCl_2$; even silicate of alumina, and of course silica itself, are supposed to act in the same way; there remain behind the silicates and aluminates of calcium or magnesium. At

least an equal weight, or more, of the earthy substances must be taken with calcium chloride; for magnesium chloride less is sufficient. Touching the practical success of this process, nothing can be heard of it. On the contrary, Franck (Zeitsch. f. d. chem. Grossgew. ii. p. 396) contends that the decomposition in that operation is very incomplete, since part of the HCl at first formed is afterwards reabsorbed, $CaCl_2$ being reformed. In any case hydrochloric acid manufactured in this way must cost so much for labour, coals, and wear and tear of apparatus, that, in all probability, it cannot compete with that obtained as a by-product in making sulphate of soda.

Hydrochloric acid is *decomposed* by electrolysis—the dry gas only to a small extent by long-continued sending through it electric or induction-sparks, partially also by heating to 1500° C. Aqueous hydrochloric acid, exposed to sunlight in a closed bottle for a length of time, gives off free chlorine, which can be detected by gold leaf after a few hours. Many other decompositions of HCl are mentioned in Gmelin-Kraut's 'Handbuch der Chemie,' i. 2, p. 379.

Dry hydrochloric acid is a colourless gas, with the density 1·2596 (calculated), molecular weight 36·457, and consists of—

	By volume.	By weight.
H	1	2·74
Cl	1	97·26

It can easily be liquefied by simultaneous action of cold and pressure; but this liquid cannot be solified even at −110 °C, and possesses a tension of 26·2 atmospheres at 0°, one of 40 atmospheres at +12·5° C. When absolutely dry it does not at once redden blue litmus paper, which after some time it chars. Hydrochloric acid has great affinity for water, and condenses with the aqueous vapour of atmospheric air into thick fumes; water absorbs it with considerable evolution of heat; and even borax, magnesium sulphate, or sodium sulphate, containing water of crystallization, absorb it from gaseous mixtures.

Aqueous hydrochloric acid is colourless, unless containing impurities; a yellow colour may be caused by ferric chloride, free chlorine, or organic substances. At the freezing-point of mercury it concretes to a butter-like mass. In the concentrated state it

fumes in the air. According to H. Deicke 1 cub. centim. of water at t° and 760 millims. pressure absorbs a number of cubic centims. of HCl gas, at the same temperature and pressure, shown in the following Table at *a*; the resulting aqueous acid has the specific gravity shown at *s*, and contains *c* per cent. of HCl.

t°.	*a* vols.	*s*.	*c* per cent. HCl.
0	525·2	1·2257	45·148
4	494·7	1·2265	44·361
8	480·3	1·2185	43·828
12	471·3	1·2148	43·277
14	462·4	1·2074	42·829
18	451·2	1·2064	42·344
18·25	450·7	1·2056	42·283
23	435·0	1·2014	41·536

Roscoe and Dittmar have examined the influence of pressure and temperature upon the solubility of HCl in water. Their table of the decrease of solubility for a decrease of pressure is given in Gmelin-Kraut's Handbuch, i. 2, 383. Their table for changes of temperature is as follows, viz. :—

1 gram of water absorbs at 760 mm. pressure :—

At 0° C.	0·825	gram HCl.
„ 4 „	0·804	„
„ 8 „	0·783	„
„ 12 „	0·762	„
„ 16 „	0·742	„
„ 20 „	0·721	„
„ 24 „	0·700	„
„ 28 „	0·682	„
„ 32 „	0·665	„
„ 36 „	0·649	„
„ 40 „	0·633	„
„ 44 „	0·618	„
„ 48 „	0·603	„
„ 52 „	0·589	„
„ 56 „	0·575	„
„ 60 „	0·561	„

Concentrated aqueous hydrochloric acid on heating loses both gas and water, and becomes weaker on boiling, till, according to Bineau, its specific gravity has attained 1·101 and its composition is 20·17 HCl + 79·82 H_2O, which exactly corresponds to the formula HCl, 8 H_2O; it then boils at 110° C., and distils without any change. On the other hand, more dilute acid on boiling loses more water than gas, till it has arrived exactly at the same point. Roscoe and Dittmar have confirmed this for pressures differing little or not at all from 760 millim., with the small correction of 20·24 HCl as the percentage of the acid distilling without change. But they found that at a lower pressure the acid distilling unchanged is stronger (for instance at 700 millim. = 20·4 per cent. HCl); at a higher pressure it is weaker (for instance at 2000 millims. = 18·5 per cent. HCl).

In the air, according to Bineau, the stronger acid gradually loses HCl till it reaches the specific gravity 1·128 at 15° C.; it then contains 25·2 per cent. HCl., corresponding to the formula HCl, 6H_2O, and boils at 106° C., with a loss of gas. But Roscoe and Dittmar have shown that here also the temperature is a decisive factor; for each temperature an acid of a certain strength remains behind, weaker at higher temperatures (tables, *loc. cit.*), which then evaporates without a change. The assumption of certain hydrates of HCl is thus without a foundation, except the hydrate HCl, 2H_2O which is formed on conducting hydrochloric acid gas into aqueous hydrochloric acid cooled down to −22° C.; in this case the gas is absorbed till suddenly the temperature rises to −18°, and the above compound is separated in crystals which, on being taken out of the cooling-mixture, at once melt and very soon give off hydrochloric acid gas.

Passing over the older Tables of Davy, Kirwan and Dalton, and Ure, we shall only reproduce the most recent one, Kolb's (Compt. Rend. lxxiv. p. 337) :—

Hydrometer.		Specific gravity.	100 parts contain at 0° C. HCl.	100 parts contain at 15° C.			
Degrees, Baumé.	Degrees, Twaddle.			HCl.	Acid of 32° Tw.	Acid of 34° Tw.	Acid of 36° Tw.
0	0	1·000	0·0	0·1	0·3	0·3	0·3
1	1½	1·007	1·4	1·5	4·7	4·4	4·2
2	3	1·014	2·7	2·9	9·0	8·6	8·1
3	4½	1·022	4·2	4·5	14·1	13·3	12·6
4	6	1·029	5·5	5·8	18·1	17·1	16·2
5	7	1·036	6·9	7·3	22·8	21·5	20·4
6	9	1·044	8·4	8·9	27·8	26·2	24·4
7	10½	1·052	9·9	10·4	32·6	30·7	29·1
8	12	1·060	11·4	12·0	37·6	35·4	33·6
9	13½	1·067	12·7	13·4	41·9	39·5	37·5
10	15	1·075	14·2	15·0	46·9	44·2	42·0
11	16½	1·083	15·7	16·5	51·6	48·7	46·2
12	18	1·091	17·2	18·1	56·7	53·4	50·7
13	20	1·100	18·9	19·9	62·3	58·7	55·7
14	21½	1·108	20·4	21·5	67·3	63·4	60·2
15	23	1·116	21·9	23·1	72·3	68·1	64·7
16	25	1·125	23·6	24·8	77·6	73·2	69·4
17	27	1·134	25·2	26·6	83·3	78·5	74·5
18	28½	1·143	27·0	28·4	88·9	83·0	79·5
19	30½	1·152	28·7	30·2	94·5	89·0	84·6
19·5	31½	1·157	29·7	31·2	97·7	92·0	87·4
20	32	1·161	30·4	32·0	100·0	94·4	89·6
20·5	33	1·166	31·4	33·0	103·3	97·3	92·4
21	34	1·171	32·3	33·9	106·1	100·0	94·9
21·5	35	1·175	33·0	34·7	108·6	102·4	97·2
22	36	1·180	34·1	35·7	111·7	105·3	100·0
22·5	37	1·185	35·1	36·8	115·2	108·6	103·0
23	38	1·190	36·1	37·9	118·6	111·8	106·1
23·5	39	1·195	37·1	39·0	122·0	115·0	109·2
24	40	1·199	38·0	39·8	124·6	117·4	111·4
24·5	41	1·205	39·1	41·2	130·0	121·5	115·4
25	42	1·210	40·2	42·4	132·7	125·0	119·0
25·5	42½	1·212	41·7	42·9	134·3	126·6	120·1

Another table, by Kremers (Poggend. Annal. cviii. p. 115) is of technical importance, showing the modifications in the volume of hydrochloric acid caused by changes of temperature. The table indicates the volume of acid of a certain specific gravity *s* and percentage *p* at another than the normal temperature of 19°·5 C.

Temperature.	Sp. gr. 1·0401, 8·9 per cent. HCl.	Sp. gr. 1·0704, 16·6 per cent. HCl.	Sp. gr. 1·1010, 25·5 per cent.	Sp. gr. 1·1330, 35·8 per cent.	Sp. gr. 1·1608, 46·6 per cent.
0° C.	0·99557	0·99379	0·99221	0·99079	0·98982
19·5	1·00000	1·00000	1·00000	1·00000	1·00000
40	1·00707	1·00781	1·00877	1·00990	1·01063
60	1·01518	1·01665	1·01794	1·01969	1·02108
80	1·02639	1·02676	1·02791	1·02986	
100	1·03855	1·03801	1·03867	1·04059	

For instance, an acid of 25·5 per cent. HCl, showing at 19°·5 the spec. grav. 1·101 = 20° Tw., will only show—

At 100° C., $\frac{1·101}{1·03867}$ = 1·060 spec. grav. = 12° Tw.

„ 80°, $\frac{1·101}{1·02791}$ = 1·071 „ „ = 14° „

„ 60°, $\frac{1·101}{1·01794}$ = 1·082 „ „ = 16½° „

„ 40°, $\frac{1·101}{1·00877}$ = 1·091 „ „ = 18° „

Hydrochloric is a very strong acid, which even in a very highly diluted state still reddens blue litmus-paper, and has a strongly acid taste. It dissolves most metallic oxides, forming chlorides, also many metals with evolution of hydrogen, especially all metals soluble in dilute sulphuric acid. Lead also, which is scarcely at all attacked by dilute sulphuric acid, is quickly corroded and dissolved by somewhat concentrated and hot hydrochloric acid; accordingly, lead vessels, pipes, &c. are to be avoided as much as possible in its condensation or employment.

Of great importance is the action exerted by hydrochloric acid upon compounds very rich in oxygen, viz. upon the peroxides of manganese and lead, chromic acid and its salts, nitric acid, &c. In all these cases, but in some only on heating, the active oxygen liberated on dissolving the metal, or by the decomposition of nitric acid, acts upon the excess of hydrochloric acid so that, together with water, free chlorine is generated. Upon this reaction is founded the industrial preparation of chlorine and the products obtained by its acid, as well as the solvent action of aqua regia (*i. e.* of a mixture of nitric and hydrochloric acids) upon gold, platinum, &c. Hydrochloric acid also expels most of the other acids from their salts; many natural silicates, especially the zeolites, and also artificially prepared ones (slags), are decomposed by digestion with HCl with formation of gelatinous silica, of course most easily the soluble silicates of potassium and sodium. Phosphoric, boric, carbonic, &c. acids are frequently liberated by hydrochloric acid. Quite recently, however, the remarkable fact has been proved (comp. also p. 4) that even sulphuric acid itself, under certain circumstances, behaves towards hydrochloric acid as the weaker acid, although, owing to its greater resistance to heat and its affinity for water, it mostly expels the latter acid. Thomsen has shown, by thermochemical experiments, that in dilute solutions hydrochloric acid possesses twice the affinity of sulphuric acid, *i. e.* that for equal equivalents it draws two thirds of the bases to itself.

Boussingault (Compt. Rend. lxxviii. p. 593) has made direct experiments on the decomposition of sulphates by HCl at a higher temperature. But most conclusive are the results obtained by Hensgen (Deutsch. chem. Ges. Ber. ix. p. 1671) from the action of dry gaseous HCl upon different sulphates. Potassium sulphate is not sensibly decomposed either in the cold or at 100°; but a little below a dark red heat almost a quantitative decomposition into chloride and free sulphuric acid sets in. Anhydrous sodium sulphate behaves in the same way; but crystallized sodium sulphate (Na_2SO_4, 10 H_2O) is by a current of hydrochloric acid gas completely converted into NaCl already at ordinary temperatures, and even at −17° C. It first melts in its water of crystallization; and afterwards the temperature rises to 53° or 55° C. Lithium sulphate was decomposed as completely, the sulphates of barium, strontium, and calcium nearly but not quite completely. Cupric sulphate, either anhydrous or containing only one molecule

of H_2O, with dry HCl seems to form an addition product of the formula $CuSO_4+2HCl$, which in dry air over quicklime parts with all its acid again, but heated in a current of air or oxygen gives off free chlorine and water, and probably plays an important part in Deacon's chlorine process.

It should be remarked that in these experiments the sulphates were exposed to a large excess of hydrochloric acid in an atmosphere of this gas. Under ordinary circumstances the reaction does not proceed in this way. When a chloride, say NaCl, is brought into contact with sulphuric acid, the HCl is, at least partly, liberated, and on raising the temperature can be *completely* expelled, because after the free HCl is expelled the SO_4H_2 can decompose a fresh portion of the chloride.

Examination of Hydrochloric Acid. see p. 269.

The ordinary *impurities* of hydrochloric acid can be detected in the following way :—

Frequently it contains *sulphurous* acid, if this was contained in the sulphuric acid, or from sulphuric acid acting upon iron or organic substances. The presence of sulphurous acid is most simply detected by means of sulphuretted hydrogen, with which it gives an opaque-white colour; for this reaction, however, Cl and Fe_2Cl_6 must be absent, which is proved if chlorine-water free from sulphuric acid causes the same opaque colour. In the presence of SO_2, stannous chloride gives a yellowish precipitate of SnS_2.

Sulphuric acid is one of the commonest impurities in crude muriatic acid; it is tested for and estimated by barium chloride. It must not be forgotten that $BaSO_4$ is soluble in a large excess of HCl, and that therefore such an excess must be saturated or removed by concentration. A rough estimation of the quantity of SO_4H_2 in crude muriatic acid can be made by comparing the opacity caused by $BaCl_2$ with that caused in acids containing a definite quantity of SO_4H_2. For some purposes muriatic should be entirely or almost entirely free from sulphuric acid—for instance, for revivifying the animal charcoal used in sugar-works.

Chlorine is frequently found in hydrochloric acid, especially if the sulphuric acid employed in the preparation of the latter contained nitrous acid. A test for its presence is a starch solution contain-

ing potassium iodide, which is coloured blue by chlorine; but it is necessary first to add some pure HCl or SO_4H_2 to the reagent in order to see whether it is not coloured blue by acidifying alone, owing to the presence of iodate.

Ferric chloride is tested for by addition of ammonium sulphide &c.; it is usually estimated by precipitation with NH_3 or by titration. It also clearly appears on evaporation to dryness, along with any soda, lime, and other refractory substances, carried over mechanically in the manufacture of sulphate, or contained in the water employed for condensation. According to Stas, even quite pure acid, which on evaporating in a platinum retort leaves no residue whatever, on evaporation in open vessels takes up matters floating in the air and leaves a yellow residue, frequently containing iron.

Bromine and iodine may occur in hydrochloric acid as HBr and HI, owing to their presence in the salt. They are tested for by adding very little chlorine-water and shaking up with chloroform, which dissolves all bromine and iodine—giving with the former a yellow, and with the latter a purple colour.

Arsenic frequently occurs in hydrochloric acid as $AsCl_3$, from the arsenic contained in the sulphuric acid. Houzeau found, on the average, 0·1 gram $AsCl_3$ in a kilog. of commercial acid; Filhol and Lacassin from 1·02 to 5·007 gram As_2O_3 (=0·8–4·28 As), Glénard 2·5 gram As_2O_3, H. A. Smith 6·91 gram As_2O_3 (=5·18As), Hjelt (from the same raw material as Smith) in pan-acid of 36° Tw. 0·66, in roaster-acid of 32° Tw. 0·14 gram of arsenic per litre. Arsenic is tested for by Marsh's apparatus—also by blackening a strip of copper, according to Reinsch, or by a voluminous brown precipitate with stannous chloride (Bettendorf). If sulphurous acid and arsenic are to be sought for at the same time, Hilger (Wagner's Jahresb. 1875, p. 445) adds iodine solution. If that is decolorized, either SO_2 or As_2O_3 is present; more iodine solution is then added until an excess of it is present; the acid is poured into a test-tube, a few pieces of zinc are added, and the tube is loosely closed by a cork to which a strip of paper moistened with silver-nitrate solution is attached. If any arsenic was present, AsH_3 is given off, and the paper is blackened; if not, the original acid is again tested for SO_2 by first precipitating the sulphuric acid with barium chloride, then adding to the filtered liquid iodine solution till the colour is permanent, whereupon, if SO_2 was originally present, a new precipitate of $BaSO_4$ is formed.

The estimation of hydrochloric acid in the free state is nearly always done by means of the hydrometer. Twaddle's hydrometer has the convenient property that its degrees for the usual strengths almost exactly agree with the percentage of HCl, as appears from the table given on p. 176. Sometimes free HCl is also estimated alkalimetrically, in precisely the same way as sulphuric acid, Vol. I. p. 44.

In the combined state, as chlorides, hydrochloric acid is always estimated by silver nitrate. If any free acid be present, this can only be done gravimetrically or by Gay-Lussac's method, *i. e.* adding silver nitrate from a burette to the boiling-hot liquid up to the point at which no further precipitate is formed. This method is somewhat inconvenient in practice, because after every addition of silver nitrate the liquid must be vigorously shaken up until the AgCl is coagulated and the liquid becomes sufficiently clear for recognizing, when more $AgNO_3$ is added, whether any further opacity is caused or not. This test consequently takes some time, and whenever possible is replaced by Mohr's process, consisting in the addition of a little neutral potassium chromate to indicate the end of the reaction: so long as all the chlorine has not been precipitated as AgCl, the addition of $AgNO_3$ throws down a white precipitate only; but as soon as all the chlorine has been removed from the solution, a further addition of silver nitrate throws down a blood-red precipitate of silver chromate, which is at once visible in the hitherto white precipitate. This very accurate and quick process is only applicable in the absence of any free acid; but if any is present it can generally be neutralized by sodium carbonate and the process carried out as before; a very slight excess of Na_2CO_3 does not sensibly interfere with the reaction.

Volhard's plan for titrating silver solutions by means of sulphocyanides (Liebig's Annalen, cxc. p. 1) can also be employed here.

CHAPTER VII.

THE CONDENSATION OF THE HYDROCHLORIC ACID PRODUCED IN THE MANUFACTURE OF SULPHATE OF SODA.

In the infancy of sulphate-of-soda-making, condensation of the hydrochloric acid was never attempted; and so long as the factories were small, the neighbours tolerated the inconvenience; but when, for instance, this noxious gas escaped in large quantities from Muspratt's chimneys in Liverpool, the municipal authorities compelled the stoppage of the works, which were removed to Newton Heath, whence they were soon again driven away.

A remedy was first sought in the erection of enormously high chimneys, up to nearly 500 feet height, in order to make the acid gas harmless by diluting it with other smoke and air; but it was found that the gas descended to the ground in compact clouds, and laid waste the vegetation for greater distances. The first attempts in another direction, viz. condensation to muriatic acid, were made in 1827 at Walker-on-Tyne; and in 1835 Losh built there long underground flues, into which water was injected by a force-pump; large wooden chambers with water-injection were also tried. Further, stone towers packed with broken glass or pebbles were tried, but not successfully. The first decided success was attained by Gossage, who, in 1836, patented the coke condensers now in general use. Strange to say, in England condensation in Woulfe's bottles (receivers), employed to this day in France, even by large works, seems scarcely to have been tried at all.

The frequently-quoted investigations of the Belgian Commission of 1855 have demonstrated beyond a doubt that dilution of the hydrochloric acid vapours with much smoke or, in the case of high chimneys, with much air, is not sufficient to prevent their noxious

effect upon vegetation *. The second part of their Report (made on February 26th, 1856, and found in an abridged translation in 'Dingler's Journal,' cxlv. pp. 375, 427) is entirely occupied with this matter, and treats of the influence of wind, of the hygrometrical and barometrical state of the air, of the temperature, topographical situation, configuration of soil, distance from the source of the gas, and so forth. The effect of the gas upon trees and hedges, especially upon their leaves, was investigated with great care. It was found that trees are attacked very unequally; and the following series was established, whose first term, the hornbeam, is most sensitive, and whose last term, the alder, is least sensitive to the gas:—

Hornbeam,
Hazel,
Stone-oak,
Beach,
Birch,
White maple,
Field-maple,
Hawthorn,
Spindle-tree (*Evonymus europæus*),
Elm,
Linden,
Blackthorn (Sloe),
Larch,
Bramble,
Ash,
White poplar,
Italian poplar,
Aspen,
Thuya,
Vine,
Plum-tree,
Apple-tree,
Pear-tree,
Cherry-tree,
Red-currant-bush,
Rose-tree,
Lilac,
Elder,
Raspberry-bush,
Spear-tree (*Spiræa ulmaria*).
Hop,
Alder,
Grey alder.

With all these trees, in the order just named, first spots appear on the leaves; and then the leaves die off altogether. But as the buds are better protected, mostly the next year's leaves come out. Even the buds, however, gradually suffer; and ultimately, after long exposure to the gases, the whole tree dies off.

Herbaceous plants suffer much less than trees and shrubs. Here also spots on the leaves are frequently found—for instance,

* Compare what has been stated in Vol. I. p. 109, concerning the effect of metallurgical smoke, principally containing SO_2, upon vegetation.

on potatoes, beans, clover, lucerne, cabbage, turnips, &c.; but the plants themselves seem to suffer only partially, and root-crops least of all. It is often asserted that cattle do not like grass which has been exposed to acid vapours. In one instance only did the Belgian Commission prove that corn was injuriously affected by the acid vapours; and that was in a field directly adjoining the works; whilst it declared that no case of damage at distances of 150 yards and upwards could be established. But the possibility still remains that, even without any spots on the leaves, a deficient crop of corn may be the consequence; and it is notorious in England that, if just at the blossoming-period of corn acid vapours from alkali-works range over a field, a large number of empty ears are afterwards met with.

The radius within which the noxious effects of acid vapours are exhibited differs very much, according to the nature of the plants, the situation of the works, the more or less perfect condensation in the same, &c.; but it is estimated by the Belgian Commission at a minimum of 600 metres (=656 yards) and a maximum of 2000 metres (=2187 yards).

From the official inquiries of the Commission as to the births and deaths in the villages within the above radius it appears to be beyond a doubt that human health does not suffer any damage under the influence of the dilute acid gases; those districts even appear to suffer less from typhoid fever than others similarly situated.

According to experiments made by Christel (Wagner's Jahresb. 1874, p. 277), the noxious influence of the hydrochloric acid vapours, escaping from an alkali-works despite the most ingenious condensing-apparatus [?], upon trees, corn, flax, beans, peas, and potatoes could be proved—on hawthorn and wild vine up to a distance of 1000 metres (1093 yards). According to direct experiments, the vital functions of the individual organs of plants were disturbed when the air contained 0·1 per cent. HCl. The action attributed by him to hydrochloric acid is an alteration of chlorophyll, followed by decomposition of the other contents and of the walls of the cells.

Sonnenschein (Dingl. Journ. cc. p. 336), at Köpnik, found a decidedly injurious effect produced upon the surrounding vegetation in the neighbourhood of the alkali-works, in spite of good condensing-apparatus [without, however, proving the efficiency of that apparatus or comparing it with that of other works].

It is undeniable that alkali-works are frequently blamed on account of their acid vapours more than they deserve, and are held liable for consequences inseparable from any coal-consuming industry. The desideratum of a "complete combustion of smoke," upon which the public and the authorities lay so much stress, will certainly not remedy this matter; for the sulphurous acid from the coals, with its noxious effect, is certainly not got rid of by complete combustion of the visible soot-particles accompanying it. The sulphurous acid originally diffused in the atmosphere is there quickly oxidized to sulphuric acid. Dr. Angus Smith found that in London a million of cubic metres of air contain 1670 grams SO_3; in Manchester, where, besides the domestic fires, the number of industrial fires is comparatively larger than anywhere else in England, the quantity of sulphuric acid rises to 2518 grams SO_3 (in smaller places where sulphuric acid is made, even to 2668 grams SO_3) in a million cubic metres of air, whilst the same quantity of air in places where no coals are burnt contained only 474 grams SO_3, probably proceeding from the oxidation of sulphuretted hydrogen given off in the putrefaction of organic substances.

A very full and the latest investigation of these subjects has been made by Hasenclever ('Chemische Industrie,' 1879, pp .225 & 275).

The notoriously injurious effect of the acids contained in the air is probably much less owing to the gases diffused in the air than to the acids precipitated in rain and dew, in which they are of course more concentrated. In dry, fine weather the effect of the acid vapours is hardly felt, the plants do not seem to take it up; but in foggy and rainy weather a much smaller escape of acid vapours often does much damage, as the author knows from frequent experience. If (according to Dr. A. Smith) rain contains 10 parts of acid in a million parts, as is the case in Manchester, vegetation altogether ceases.

Although, however, even the contamination of air with sulphuric acid, inevitable with the consumption of large quantities of coal, is bad enough for the vegetation, and although the damage resulting therefrom is frequently attributed unjustly to the neighbouring alkali-works alone, the fact remains that the hydrochloric acid vapours escaping from the latter are much worse than the sulphurous acid from ordinary fires; but where large quantities of SO_2 are evolved, which soon passes over into sulphuric acid (as by coke-ovens, copper-works, zinc-works, &c.), there matters are much

worse again than near alkali-works. Even in dry air hydrochloric acid seems to be diffused much less easily and to remain longer in the state of continuous clouds than SO_2 or SO_4H_2; and in damp air hydrochloric acid escaping forms thick clouds, or, in the case of chimneys, long streams, which are only very slowly dispersed where they touch, and there exert a so much the more concentrated injurious action.

Accordingly we need not be surprised that the attempts which were made in the infancy of alkali-works to get rid of the then valueless hydrochloric acid by means of high chimneys had speedily to be relinquished *. In the first instance attempts were made to carry away the gaseous current underground—for instance, by James Young, Vivian, Losh (as above mentioned), &c.—and to wash the acid out by injected water. These flues did very little good, because it is a difficult task to keep a horizontal current of gas damp throughout its whole length; moreover the water quickly falls through the gas, and has no time to act upon it in the desired way.

The next step was taken at Liverpool by Hill and Lutwyche, viz. erecting very large *underground tanks* to absorb the acid vapour by surface contact; but in order to do this perfectly a very large surface is needed, and only weak acid is obtained. This process is accordingly quite out of date as a sole means of condensation; but the combination of smaller tanks with proper coke-towers has turned out very suitable, as we shall see later on.

The only really sufficient appliances for condensing hydrochloric acid are the series of *Woulfe's bottles* (receivers—in French "bombonnes" or "touries"), mostly employed on the continent, and, still more efficient, the *coke-towers* invented by Gossage in 1836. Of late years, frequently, tanks, receivers, and coke-towers have been combined so as to form a set. Already in 1846, Gossage's coke-towers were universally employed in English works; but, as generally constructed, they were very inefficient; and in consequence of their unsuitable construction and that of the de-

* A very practical (!) proposal was patented to a Mr. Edward Ford on March 8, 1839, which the author has not found mentioned anywhere, but which should not be concealed from a grateful posterity. The furnaces &c. were to be sufficiently far removed from the mainland not to injure vegetation; and a ship or flotilla, partly lined with lead, was to be moored on the high seas, and the works erected upon it. For this patent the full tax was paid!

composing-pans, furnaces, and conducting-pipes, there were still enormous quantities of uncondensed acid vapours sent into the air. Before 1862, according to an estimate of Fletcher's, ten factories in Lancashire alone poured forth weekly 255 tons of dry HCl, and all the English factories together at least 1000 tons, or upwards of 800,000 cubic metres. According to Dr. A. Smith, the usual loss of HCl in sulphate-making was then 16 per cent. on the average, but 40 per cent. in some cases. In Belgium the Commission of 1855, as can be calculated from their Report (p. 57 *et seq.*) found even greater losses, viz. in the four factories examined, 43·2, 28·3, 56·9, and 44·4 per cent. of the HCl yielded by the salt. In France Freycinet calculated, in 1866 ('Rapport du Jury International,' 1867, vii. p. 42), that at that time one half of all the hydrochloric acid generated went into the air.

It is no matter of surprise that, under these circumstances, the complaints about nuisance were quite as great as at the time when no hydrochloric acid at all was condensed; for in the meanwhile alkali-works had increased to such an extent that the absolute quantity of hydrochloric acid escaping uncondensed amounted to much more than that which escaped in the former period, when no condensation at all was attempted. The destruction of the vegetation round the alkali-works was only too evident, without any Commissions of inquiry, although it is a matter of fact that, on the whole, the value of land round the works had increased (12th and 13th Reports, p. 15). It was impossible to ignore the nuisance caused by the smell, and the worse one that iron objects of all kinds, locks, window-fittings, gutters, &c. could not be kept from rusting, that the tools of mechanics were at once blunted, and that even window-curtains were destroyed in a very short time. The public, thus afflicted, can hardly be blamed if they raised the reproach, unjustified as it was, that the alkali-works poisoned the air of the neighbourhood and caused diseases; and although exact investigations have, on the whole, disproved the accusation (see the author's paper in the 'Transactions of the Newcastle Chemical Society' for 1874), no doubt many individual cases have occurred where already existing affections of the respiratory organs and the like have been aggravated by breathing the acid vapours of neighbouring alkali-works, where sufficient care had not been taken to condense all the noxious vapours.

The most potent incentive to preventing any waste of products in

factories seems always to be the fact that it entails pecuniary loss. But experience has proved in innumerable cases that it does not suffice for preventing such waste: the convenience of many manufacturers, on the one hand, and their employés' insufficient knowledge, on the other hand, have been more than sufficient to counterbalance it. Even the intervention of the courts of law, the claims for damages, and other unpleasantnesses of all kinds, could only in isolated cases prevail to bring about a thorough cure. The worst was that, as a rule, in this case a pecuniary motive for preventing the escape of hydrochloric acid did not exist; fifteen or twenty years ago only a small portion of the hydrochloric acid generated in alkali-making could really be brought into the trade as such, or used up in the factories themselves for making bleaching-powder, chlorate of potash, and bicarbonate; of the remainder, all that did not go into the air had, after condensation, to be run into the nearest water-course, where it killed all the fish and gave rise to fresh complaints.

It was therefore inevitable that in the end *legislation* should intervene. In Belgium this was done in a seemingly thorough and scientific, but in fact in an unsuitable way. Open roasters for calcining sulphate were prohibited, and muffle-furnaces were made compulsory, but without at all stopping the nuisance, just because blind roasters themselves, as we saw in Chapter IV., are any thing but trustworthy. Chandelon found in 1871, when inquiring into this matter, that the four factories, which he and his colleagues had visited in 1855, condensed the following quantities of HCl, calculated upon 100 kilog. salt:—

	In 1870.	In 1855.	More in 1870.
I.	174·7	108·8	63·9
II.	146·57	74·50	72·07
III.	117·0	58·7	58·3
IV.	113·0	74·5	38·5

But since in 1870 more than twice as much salt was decomposed as in 1855, the absolute losses were still very great.

In England legislation has proceeded in another, and, it would appear, in a more successful way. The law of 1863 (usually called Lord Derby's Alkali Act) does not prescribe to the manufacturers any thing about the apparatus which they have to use; but it makes it incumbent upon them to allow at most 5 per cent. of

the whole hydrochloric acid given off to escape into the atmosphere; and it established a compulsory registration and periodical inspection of all factories manufacturing sulphate. The generation of hydrochloric acid in the wet copper-extracting process, little known at that time, was passed over. An additional Act of 1874 now includes the latter, and moreover prescribes that in a cubic foot of the gas escaping from the factory into the atmosphere no more than 0·2 grain of HCl may be present; this equals 0·454 gram HCl per cubic metre, or about three ten-millionths by volume (comp. next page).

After three years' working, Lord Derby's Act already showed that a practically complete condensation of all the HCl escaping in the manufacture of sulphate was not merely possible, but even easy. Whilst Dr. Angus Smith calculates that immediately before passing the Act about one third of the HCl generated went into the air, at the end of the first year the actual condensation was, on the average, 98·72, the loss only 1·28 per cent. In the second year the average condensation was 99·11, the loss 0·88; in the third year the condensation was 99·27, the loss 0·73.

Dr. Smith himself points out that, apart from the inevitable inaccuracies of the testing-processes, a certain amount of HCl always escapes without being accounted for, and that consequently the above figures cannot lay claim to absolute accuracy. The English inspectors proceed thus:—They aspirate a certain volume of air from the pipe or flue through which the acid vapours escape from the furnace, and estimate the amount of chlorine contained in it. A similar quantity is aspirated from the pipe leading from the condensers into the atmosphere or towards the chimney; and by estimating the chlorine it is found whether any, and how much, HCl has escaped condensation. Thus, necessarily, all the HCl which is given off by the finished sulphate as it is drawn out of the furnace is neglected. Dr. Smith estimates the loss from this source as never exceeding 1 per cent. It might be entirely prevented by drawing the salt into arched caves communicating with the condenser, and allowing it to cool there. That this is not done in the English alkali-works, and why, we have seen on p. 124. Even without these caves the escape of vapours from fresh sulphate can be almost entirely prevented by the little artifice already mentioned, covering the red-hot sulphate immediately with a few spadefuls of cold sulphate. If, as is usually the case, more sulphuric acid has been

employed than is absolutely required, the vapours escaping consist mostly of sulphuric acid, and, properly speaking, do not come under the Act. Another source of loss of hydrochloric acid are the leaks in blind roasters, by which a little acid is drawn into the chimney instead of through the condenser; nay, a case is said to have happened in which a special flue was built purposely for taking away a portion of the gas straight to the chimney. Apart from its legal and moral criminality, such a proceeding would, in most places, appear to be even economically absurd; but in special local circumstances it still happens that the condensed acid must be run to waste, partly or entirely, and that condensation is thus a burden instead of an advantage. Since the Act of 1874 prescribes testings of the chimney-gases themselves, such cases would be detected very soon, and can scarcely happen now.

So much is certain, that even those alkali-works which figure in the reports as "completely condensing" are still distinctly perceptible to the sense of smell. It is certainly sometimes difficult to decide how much of the "alkali-smell," as the people call it, is owing to HCl, and how much to SO_2, Cl, and H_2S. (These matters have been very fully investigated by the Noxious-Vapours Commission, 1876–78, whose report is briefly summarized in the 'Chemical News, vol. xxxviii. p. 181; it cannot be said that any thing essentially new is contained in it.)

An addition was made to the Alkali Act in 1874, when, apart from including within its operation a number of works previously excluded, the escape of noxious vapours generally was prescribed to be kept within the narrowest possible limits, and that of hydrochloric acid especially was limited to 0·2 grain per cubic foot of the chimney-gases—thus establishing an altogether new requirement, which was at first declared by many manufacturers to be impossible of fulfilment. But it appears, from the 12th and 13th Reports by the Inspector (p. 8), that the actual escape in 1876 only averaged 0·12, 0·105, 0·141, and 0·123 grain per cubic foot in the four districts into which the Kingdom is divided for the purposes of the Act.

The enormous progress in condensation realized by the English alkali-works in the first year of the Alkali Act proves how easily that object is attained if the principle of condensation is clearly understood. This can be reduced to three conditions—sufficient water, large surface for contact, and well cooling. The condensing-apparatus ought to be constructed in such a way that the gas will

not require more water for complete condensation than is sufficient for yielding strong acid; and this is attained partly by large surfaces (coke), partly by air-cooling. The importance of this last condition especially has been more and more recognized; Dr. Smith calls the cooling of the gas previous to entering the condensers "the key of every good condensation." Some works in Germany and France even employ an outer cooling of the condensing-apparatus by means of cold water; this is not practised in England, and seems unnecessary.

Whilst not merely the weighty authority of Angus Smith, but the uniform experience of all practical men hitherto has advocated the utmost possible *cooling* of the acid gas before exposing it to the condensing action of the water, Schloesing (patent of Feb. 13, 1878, No. 613) believes he has found in precisely the opposite quarter the proper way to condense. According to him the cooling deprives the gas of its tension, so that it is brought into contact with the absorbing medium (water) merely by mechanical means, requiring a long path for complete action; but if a certain tension is kept up, the absorption itself maintains a continuous current of the volatile body towards the absorbing surface. Schloesing therefore allows the gas to retain a temperature much above 100° before entering the condensers, and regulates the feed of water so that it remains just liquid, while the temperature of the tower is 100°. Even at nearly 100° he expects the water to absorb sufficient hydrochloric acid for the stable hydrate, boiling at 108° C., of 18·5 per cent. HCl, to be formed. The towers may be 10 or 20 times smaller than at present without a trace of hydrochloric acid escaping.

This reasoning appears to be utterly fallacious. It is incomprehensible how Schloesing could forget:—first, that, real hydrochloric acid being a gas at the ordinary temperature and far below, it is quite unnecessary to impart any "tension" to it for the purpose of bringing it into enlarged contact with the absorbing medium; secondly, that there is a vast difference between liquid acid *retaining* 18·5 per cent. HCl at 108°, and water *absorbing* that quantity at nearly the same temperature, seeing that the absorption causes a considerable rise of temperature; thirdly, that acid of 18·5 per cent. HCl is too weak for most purposes. The assertion that with Schloesing's system $\frac{1}{10}$ or $\frac{1}{20}$ of the present absorbing-space is sufficient for complete condensation of the hydrochloric acid, seems to rest on mere hypothesis. As his plan is going to be put to a

trial at a factory in the north of France, it will soon be known what there is in it.

Schloesing applies the same principle to the condensation of *sulphuric* acid contained in gases; but as this acid does not possess any considerable tension below 160° C., he recommends passing the gases through a tower filled with lumps of common salt and kept at 300° or 400° C. At the bottom melted sulphate flows out, whilst hydraulic acid escapes and is condensed in an apparatus similar to the above-described condensers.—The utter impracticability of this plan is self-evident to anybody who has ever seen or heard of the difficulties caused in Hargreaves's process by any fluxing of the salts.

Nitric acid and *ammonium carbonate* (in the manufacture of soda by the ammonia process) are, according to Schloesing, to be dealt with in the same manner.

The condensing-apparatus ought to be, if possible, simple and not very liable to get out of repair. Receivers (the number of which in a large factory would amount to many hundreds, as it actually does in France and Germany) are employed in very few of the English works. Bombonnes by themselves, without coke-towers, can hardly effect complete condensation. The advantage offered by them, viz. the production of pure and strong acid, and good cooling by air, can be secured by simpler and more lasting apparatus, viz. stone cisterns. The best plan for combining complete condensation with the production of the strongest acid seems to be a combination of bombonnes and coke towers.

It cannot be denied that some factories attain good condensation even with the neglect of some very commendable precautions. The author knows a number of factories where the gas is carried direct into the condensers by underground flues, without any cisterns, and yet nearly or quite perfect condensation is obtained. But then their towers must be wider and higher than would otherwise be required. This would not matter so very much, if it did not follow that the acid is less concentrated and more dilute, and can very rarely be utilized to the full extent.

The task of condensing the hydrochloric acid is different, according to whether the whole or most of the acid is to be brought to saleable strength, or only sufficiently concentrated for own use, or merely to prevent the escape of any HCl into the air, without any regard to the strength of the condensed acid, as the latter is anyhow partly or entirely run to waste. The latter case, although rare, still

happens; the first case is still exceptional in England, but pretty frequent on the Continent; the second case, where the condensed muriatic acid is almost or quite all used up at the works, is the most frequent one in the large centres of alkali-making. The condensing-appliances must necessarily be chosen differently, according to whether one or the other of the above cases has to be provided for; and this difference must already begin with the choice of the apparatus for decomposing the sulphate itself.

If the task is that of bringing all condensed acid to 32° or 36° Tw., none but blind roasters can be employed, and, in condensing, either stoneware receivers or cisterns must be added to the towers, so that not only the pan-acid, but also the roaster-acid can be made strong enough. If one third of the acid corresponding to the yield of the roaster can be used up at the works, open roasters may be employed, if fired with coke; with proper appliances they furnish acid of 22° to 26° Tw., which is quite suitable for chlorine-making. If the roaster-acid is not wanted at all, or only in the state of weak acid (for instance, for bicarbonate), the open roasters may even be fired with coals; but then the condensers must be packed with bricks and very loosely, so as not to be stopped up by soot, and the condensed acid will only show from 3° to 6° Tw. The condensation of the two thirds of acid escaping from the pan will of course take place exactly as in the first case. It happens only exceptionally that even the pan-acid cannot be utilized and must be run to waste; and in this case the furnace shown in figs. 35 and 36 on p. 72 can be employed.

With open driers, separate condensing-apparatus must always, except in the case just mentioned, be provided for the pan and the furnace: from the first equally strong acid is obtained as by any other process; from the second, even by firing with coke, rarely any thing above 22° to 24° Tw., frequently less than that; and whilst the pan condensers may be in direct communication with the air, of course the roaster condenser, through which all the fire-gases pass as well, must be connected with a chimney.

In the case of blind roasters it is an open question whether to employ special pipes, condensers, &c. for pan and roaster, or not. Frequently both currents of gas are united and sent into the same tower. This, however, does not seem to be the best plan. The pan-gas is much more concentrated than the muffle-gas, since during the turning over of the charge a good deal of air is carried

through the open working-doors into the muffle; and in any case the latter gives off much less gas in the same time and for the same cubical space than the pan. Moreover the pan-gas is much cooler and more easily condensed. From both causes the pan-gas is more easily dealt with than the roaster-gas, and it does not seem rational to mix them, instead of erecting special condensing-apparatus for each:—simple fireclay or glass pipes and tightly packed condensers, open at the top, for the pans; and, on the other hand, longer and wider cooling-flues, partly of metal, partly of stone or fireclay pipes (preferable to brick flues), along with more widely packed condensers, connected with the chimney, for the roasters. The latter is recommended because the roaster requires a stronger draught to prevent the gas from blowing out of the working-doors. In case of need the same coke condenser can be used for both gases, after the roaster-gas has been cooled down to the temperature of the pan-gas; but even then one advantage is sacrificed which the separation of the gases affords and which in some cases is very valuable, viz. collecting the purer pan-gas, nearly free from sulphuric acid, separately from the much less pure roaster-gas. We will cite some special instances.

At St. Rollox the arrangement is stated, by E. Kopp, as follows (the new works of Messrs. Tennant at Hebburn-on-Tyne possesses open roasters and consequently a totally different condensing-plant):—viz. the pan-gas travels through a stoneware pipe 15 inches wide, first 17 feet upwards and then, descending gradually to the condenser, a length of 125 feet. The gas of the roaster (the furnace is 15 feet wide and 30 feet long outside) travels through a pipe of 12 inches (?) diameter the same way as the pan-gas, and into the same condenser; but the two gases are mixed only inside the latter. Each condenser is 6 feet square by 46 feet high, apart from a foundation of 6 feet and the house for water-cisterns &c.

At Messrs. Chance's, at Oldbury, the gases likewise mix in the condensers, of which there are always two combined, so that the gases ascend one and descend the other (this is not a good arrangement) and at last pass through a small chamber, which can be entered by a man in order to satisfy himself of the progress of condensation. Each tower is 3 feet 3 inches square, and has a working height of 36 feet. Both those plants (which may have been altered since) would now-a-days be called partly obsolete.

It seems more rational, if several decomposing-furnaces are present, to restrict the number of condensing-towers by conducting the gas of two or even more pans into one, and that of the corresponding roasters into another. Of course the condensers must be made larger, in proportion to the larger volume of gas; but in this way the condensers are more evenly worked than if each pan has its own tower. In the latter case, shortly after charging the pan much more acid vapour will rush into the tower than later on. Properly speaking, in the beginning much more water ought to be run down the condenser than afterwards; but this is not practicable, on account of the great trouble it would give. If, however, the gases from two pans go into the same condenser, their charges will be so timed that, with hourly charges, the gas from one pan will always come half an hour after that from the other; the principal evolution of gas in the first pan will be already over when it begins in the second, and so forth. Thus there will be a much more equal mixture of gases in the condenser, and there will even be a considerable saving of condensing-space; for as the condenser must always be large enough to receive and properly condense the maximum of HCl given off, but with two pans the maximum of one coincides with the minimum of the other, there will be much less space required for a common condenser than for separate condensers for each.

It is true that the above-mentioned interval of half an hour is not always easily adhered to; for since the pan-men have to wait for the roaster-men getting their charge finished, and the latter cannot always finish in time, disputes frequently arise between them, and the men have to be carefully looked after in this respect. The proposal of Kopp, to group *four* pans together, which would have to be charged at regular intervals of 15 minutes each, is altogether impracticable for the same reason. When the pans are not charged hourly, but at longer intervals, a regular rotation between them is much more easily carried out.

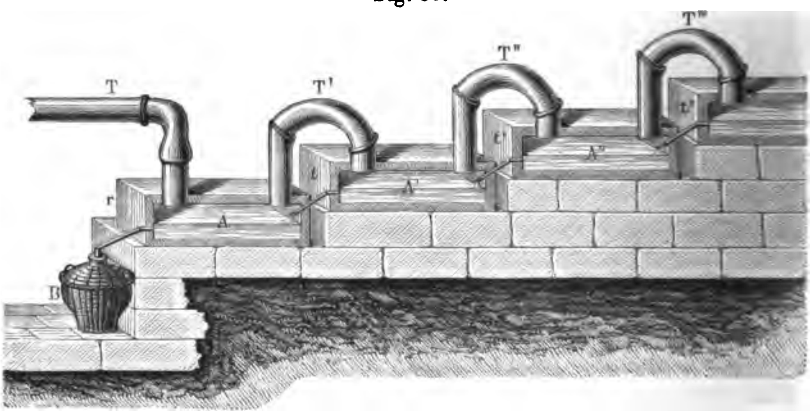
More rarely than for two or more pans or close roasters a common condenser is met with for two or more open roasters: in this case the evolution of gas is at any rate much more regular, especially since the proportion of acid vapour in the fire-gas is comparatively small.

In the case of stoneware receivers there are always separate strings of bottles for each pan and for each roaster.

Description of the Condensing Appliances in detail.

We have seen above that at first the condensation of the hydrochloric acid gas was attempted by means of *tanks* filled with water, over whose surface the gas was conducted. In order to *completely* condense any quantity of hydrochloric acid in this way, the water-surface should be very large indeed; and this is all the more troublesome as metal or wood vessels cannot be employed, and even brickwork set in pitch stands very badly; so that ultimately only the very expensive stone tanks remain available. Not only on account of the cost, but also of the large ground-space required, this condensing-arrangement would be practically impossible for any large factory. The tanks themselves are moreover very unsuitable, because they only furnish weak acid, except when mounted in terraces, as in fig. 99. Such tanks are made in France from the

Fig. 99.



Vosges sandstone, usually in one piece, with walls 8 or 10 inches thick and boiled in coal-tar; they are usually about 6 or 7 feet square and 2 feet high. They are filled two thirds with water, which from the higher tanks A'' flows over to A' by the overflow-pipes *t t t*, afterwards to A, whilst the gas entering at T travels the opposite way by means of the siphon pipes T', T'', T''', and thus better saturates the water with gas. At the bottom at *r* somewhat concentrated acid ought to run into the carboys B.

A very large number of such tanks would have to be employed if the acid had to be *completely* condensed by them *alone*, and, in

spite of this, no very strong acid could be obtained. Therefore tank condensers went out of favour; and, in England especially, even now they are less employed than they deserve to be, if used in the proper way, viz. only as supplementary to coke-towers. We shall go into this afterwards; here we shall only describe the construction of such tanks; and we remark that these constructive details also apply to stone condensing-towers.

Different systems may be employed for constructing stone tanks. In France and Germany they are sometimes hewn out of one large block. This for large sizes is enormously dear; and if the tanks crack, it is often impossible to repair them. We shall therefore only enter upon the two constructions usual in England, and represented in figures 100–108.

Fig. 100.

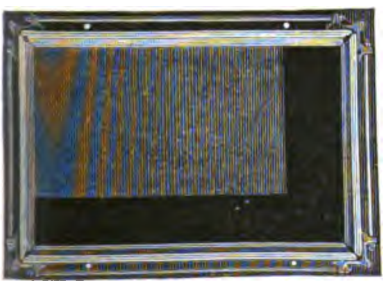


Fig. 101.

Fig. 102.

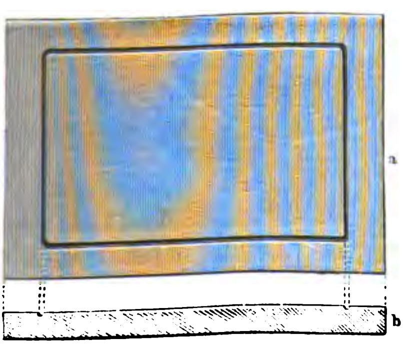


Fig. 103.

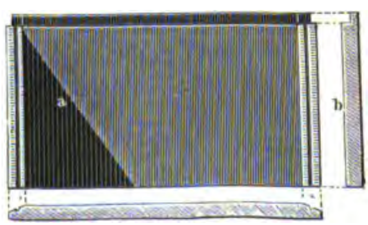
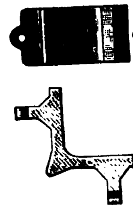


Fig. 104.



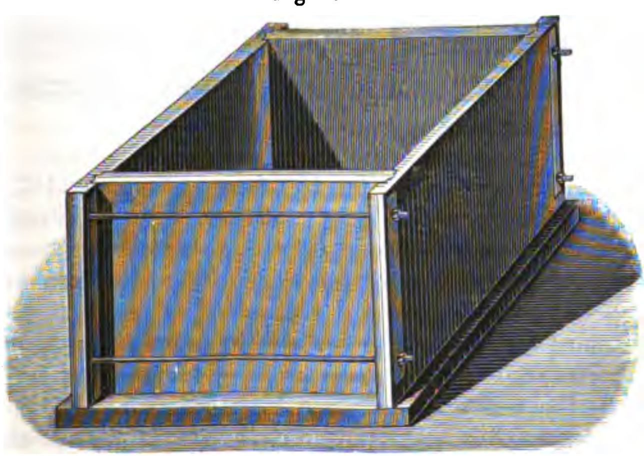
In the first construction the edges of the sides are bevel-jointed; they are bound together by cast-iron brackets and tightened by india-rubber cord. Fig. 100 shows such a tank as viewed from above, after taking away the cover; fig. 101 is a side elevation, fig. 102 the bottom-stone, and fig. 103 one of the four side-stones as they have to be dressed by the mason; fig. 104 *a* is a side elevation, and *b* a horizontal section of a corner bracket. In the bottom-stone a shallow groove, 1 inch broad × ¼ inch deep, is made in the middle of the place intended for the side stones, for receiving the india-rubber cord. As the stones are rarely sufficiently even, a band of 6 inches width is first dressed smoothly all round the stone, and the groove cut into this afterwards. The side stones are dressed quite smoothly below, and a similar groove is cut in. Their two lateral edges are dressed as shown in the diagram; but only the bevelled part, which has to receive the groove for the joint, must be dressed smooth. The upper edge receives a recess for the cover. This itself does not require any dressing; it may also consist of two halves, while the bottom-stone must not. The cover is provided with a man-hole. When the bottom has been dressed and placed exactly level on its bed, an endless ring of 1-inch solid india-rubber cord is put into the groove, to whose square shape it is, of course, easily fitted, and is fixed at the four corners by tacking down. In these corners afterwards, by cutting in, ⅝-inch india-rubber cords are fixed, equal in length to the height of the sides; they afterwards serve for tightening the side-joints, and in the meanwhile are held by strings from the top. The four side-stones are singly put into their places and fixed by wedges a little above their final position, so that they all incline outwards against wooden props. They are then carefully put into their proper places, exactly plumbed, and the horizontal and vertical india-rubber cords drawn into their grooves, whereupon the wedges are

drawn out and the weight of the stone is allowed to press upon the india-rubber. The sides still remain supported, till they have been bound by the brackets, and held together by 1-inch round screw-bars. The binding is troublesome work, since every single piece has to be supported till the last bolt is in its place. Where the brackets touch the stones, small recesses are cut in and strips of lead put between the stone and the cast-iron bracket, which equalize the pressure.

Now the cover is put in, and the joint made good in its recess by tar and china-clay; if it consists of two halves, the joint is made in the same way. The pressure of the sides on the india-rubber cord is not sufficient to make the tanks acid-tight; therefore two cross bars (about 4 inches × $1\frac{1}{2}$ inch) are put on the cover, through whose ends pass screw-bolts, which bend off at a right angle below the bottom-stone, and on screwing the nuts down hold the cover, sides, and bottom tightly together. In fig. 100 the places are visible where these four perpendicular bolts are fixed, and in fig. 101 one pair of these along with the cross bar.

In the second construction two opposite sides fit into grooves of the end-stones at right angles with them; all four rest in grooves of the bottom-stone. The binding only takes place from one end to another by means of long bolts connecting the projecting parts of the end-stones; and the joints are always made good by tar and china-clay cement caulked in. Fig. 105 shows a tank of this kind

Fig. 105.



in perspective, but preserving the proper dimensions. Only, in order to show clearly the way in which the sides and ends are feathered and grooved together, the upper recess, which must be made for the cover-stone, has been omitted. Fig. 106, *a*, shows the

Fig. 106.

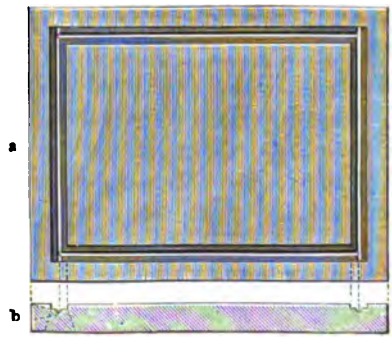


Fig. 107.

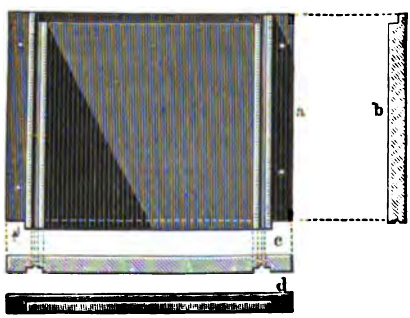
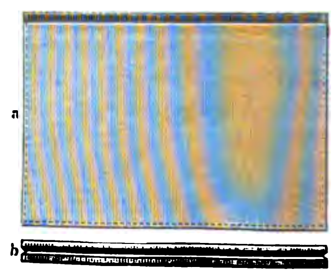


Fig. 108.



bottom-stone from the top; fig. 106, *b*, in section; fig. 107, *a*, one of the ends, seen from within; fig. 107, *b*, the same in side elevation; fig. 107, *c*, top-elevation; fig. 107, *d*, bottom-elevation. The recess for the cover is here shown, figs. 106–108 being working-drawings for the stone-mason. Fig. 108, *a*, is an elevation of one of the same; fig. 108, *b*, the same from below. In fig. 106 are seen the grooves for the sides and ends, $4\frac{5}{8}$ inches broad and 1 inch deep. In the middle of each is a V-shaped groove (1 inch side), which, together with a corresponding bottom-groove of the sides

and ends, forms a channel for the cement. The two outer parts of the ends, where no joint is necessary, are left rough at the bottom, and are perforated with two bolt-holes each. Besides, the ends have each a perpendicular groove, $4\frac{5}{8}$ inches wide and 1 inch deep, with a V-shaped recess in the centre, just like that in the bottom; the edges of the sides enter into this groove. The sides themselves only have a V-shaped recess all round the two sides and the bottom, since they enter with all these into the grooves of the ends and the bottom—and moreover a recess for the top-stone on their upper edge. The thickness of the sides and ends in this case is assumed $=4$ inches, so that the grooves are wide enough for caulking with some cement.

If a tank of this kind has to be put up, the bottom is levelled, the sides and ends are placed a little above their final positions and provisionally supported. Then the bottom grooves are completely filled with tar and china-clay cement, and the sides and ends let down into them; of course a great deal of cement is squeezed out, and is stemmed inside and outside into the space left between the stones and the margins of the grooves. First, however, two days are allowed to elapse, for the cement to harden a little. For the upright joints the process is somewhat different. The cement is made into small balls, which are dropped into the lozenge-shaped groove, and rammed down with a hot iron, a good deal of cement getting squeezed out sideways; this is continued till the top is reached. Here also the cement squeezed out is stemmed into the small joints remaining in the grooves. The four screw-bolts connecting the two ends are put in and are tightened up as much as possible. In order to divide their pressure all over the stone, they press upon an iron bar 4 inches $\times$ $\frac{3}{8}$, or upon a piece of pitch-pine 4 inches $\times$ 6. The cover may be simply bedded in cement in its recess; the cross bars and vertical screw-bolts are not required here, as the bottom-joint is tight without them. This, however, only holds good of the acid-cisterns, with which we are occupied at present; in the case of the chlorine-stills, otherwise built in exactly the same manner, it is safer to screw the top down, on account of the steam-pressure.

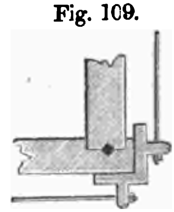
The question now is, which of the two systems just described is preferable to the other. In the first system a somewhat smaller stone surface is required for the same cubical contents, and the dressing of the stones takes less time, because the large grooves

have not to be made; the bevelled edges, also, certainly take a good deal of work. On the other hand, much more iron is required than in the second system, viz. eight screw-bolts instead of four for the sides, eight corner brackets, and the cross bars and screw-bolts for the tops. Once complete, these cisterns last very long without any repair; but if they have to be taken to pieces, the india-rubber cord cannot be used again. With the second system more stone, and labour for cutting, are required, but a little less labour for putting them up; the saving in ironwork is very considerable; and the tar and china-clay cement is also much cheaper than the india-rubber. The joints are not quite so much to be depended upon as in the first system; and stemming the joints is now and then necessary. Every thing here depends upon the care and skill of the first builder; the author has known stills of this kind which after five years' use did not show any signs of leaking.

The tanks, according to the second system, are on the whole somewhat cheaper than those on the first. The first system is principally used in Lancashire, the second on the Tyne. It would appear that there is not much to choose between them; but the author would prefer the second (groove-joint) system even for acid-cisterns and stills, and quite decidedly for condensers.

A combination of both constructions consists in employing grooved joints and tar and china-clay, but joined by corner brackets and the same number of screw-bolts as in the bevel-joint system. The sketch (fig. 109) will make this clear. This style was selected in a special case from fear that the direct pull of the bolts upon the projecting ends might be too strong; but later on the author found the stills built just in the manner illustrated in figs. 105 to 108, with grooved joints.

Fig. 109.



Thus far we have not regarded the thickness of the stones, which indeed depends upon various circumstances. In the north of England "Yorkshire flags," from Halifax and Southowram, are very much used, consisting of a sandstone that resists hot acids even without boiling in tar, which, on account of its dense grain, would not do it much good. It splits very evenly; so that flags of large size and of any thickness can be obtained by the simple use of the wedge. Of this stone much thinner slabs can be used than of more

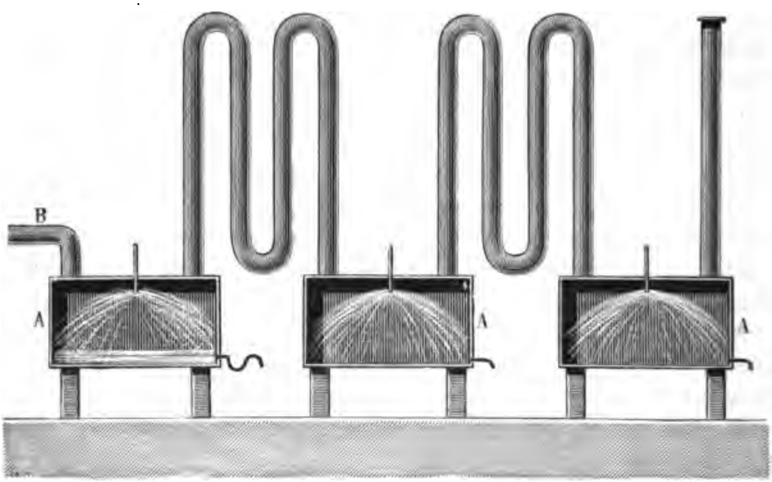
porous and less firm sandstones, of which thin plates are frequently as dear as or dearer than thick ones. A thickness of 6 inches for the bottom, 4 inches for the sides and ends, and 4 or even 3 inches for the tops will do; frequently thicker stones are employed, but without any good reason. Although this stone is not boiled in coal-tar, it is useful and costs very little to paint the tanks well with tar or, still better, with varnish made from tar.

In the Tyne district also a very good siliceous sandstone is found, which is employed for acid-tanks, condensers, and chlorine-stills. Its denser varieties, such as the Heworth stone, do not require boiling in tar. This stone does not split in plates, and must be cut out of the rough; it is rarely employed below 6 inches, usually 7 inches, for the sides, and 10 to 12 inches for the bottom. It is not so readily cracked by changes of temperature, and does not scale off under the influence of hot acid, as Yorkshire stone does in the course of time. A similar stone is found in Germany, near Herdecke and Wetter in Westphalia.

Any open varieties of stone must *be boiled in coal-tar*, always *after* being dressed by the stone-mason; for a sandstone after boiling in tar is too hard to be cut. For this purpose an iron pan is used, over which a travelling crane runs for putting in and lifting out the stones. The tar must be deprived of its most volatile constituents by boiling; but it should not be boiled down to a very thick consistence, because the pitch thus formed will not penetrate sufficiently into the stone. The stones (or the whole tanks if made in one piece) must be left lying at least a week in the boiling-hot tar. Even then the tar barely penetrates half an inch into the stone, but still imparts to it great resistance against acids, as well as against changes of temperature, rendering it as it were tougher.

Instead of simply filling the acid-cisterns with water, and thus acting upon the gas only by a condensing surface equal to the horizontal area of the tank, Newall and Bowman (patent of June 15th, 1874) have applied a principle long before known for cooling and washing gases, viz. a very finely divided spray of water. The novelty of their process only consists in the way in which the spray is generated. Fig. 110 will show this more clearly, along with the following description.

Fig. 110.



The gases are introduced into stone cisterns 6 feet × 6 feet and 2 feet high: here the gas meets a spray of water filling the whole space of the trough in the shape of a fine mist, which washes the HCl out of the gas very quickly and completely, so that twelve such sprays are to suffice for four decomposing-furnaces. In this operation the latent heat of the HCl vapour becomes free; and the temperature of the gas is very much raised thereby. The gas must therefore be introduced by a number of comparatively small pipes, in order to get as much cooling-surface as possible, and the pipes must be bent upwards and downwards between each two tanks; behind the last tank a small coke condenser should be placed about one quarter the size of an ordinary condenser. The acid in the cisterns gets a strength of 33° Tw.

The principal condition is the generation of a sufficiently fine mist, which is obtained by allowing the water to run, under a pressure of nearly three atmospheres, through a platinum nozzle of $\frac{1}{16}$ inch bore onto a small button of platinum fixed $\frac{1}{8}$ inch below it, from which the jet is thrown back and a very fine dust of water generated. Since the fine outlet of the nozzle is easily stopped up, the water should be filtered. Of course, in lieu of water, dilute acid may be used. The inventors expected that their tanks would not interfere with the draught to the same extent as coke-towers, and that the process would therefore be applicable in many other

cases—for instance in washing copper and lead smoke, in the scrubbers of gas-works, &c. It has not, however, fulfilled the highly wrought expectations with which it was at first welcomed. It has been tried in several places, but given up again. The main difficulty is that, in consequence of the very high pressure and the fine openings (both indispensable for producing a mist), the orifice of the nozzle is constantly getting stopped up, even if filtered water be used, which in itself is a very onerous condition.

Possibly Felsinger's "mist-pump" would better suit the purpose. In this the mist or spray is produced by the action of compressed air (described in 'Praktischer Maschinen-Constructeur,' 1878, p. 254); but this involves both the employment of driving power for compressing the air and a dilution of the gases by the latter.

Condensation in *Woulfe's bottles* or *receivers* (bombonnes, touries) is hardly at all employed in England; but in France, Germany, Austria, and Belgium it is the most usual plan, partly with, partly without a small coke-tower at the end. Most good works have the latter as well.

The receivers are large stoneware bottles, provided with two large necks and one small one on the top, and with a short branch for a tap at the bottom, mostly also with side branches for mutual communication. It is very important that both in the manufacture of the receivers and in the previous separation of the clay the greatest care should be exercised. Of course the clay should be entirely free from lime; it must moreover be well levigated lest any small pieces remain in it, which already in burning, or, if not then, certainly afterwards in use, give rise to cracks. Even then not all kinds of clay are adapted for this use, but only good, fire-proof kinds. In moulding and burning also the greatest care must be taken. On burning, the heat, as with all real stoneware, must be increased up to the point at which the mass frits and is semivitrified; even without an enamel it should not allow any liquid to pass through; and of course it should have no cracks. After all, such receivers as really fulfil all fair requirements and do not crack by changes of temperature, can only be got from a few places. In America, for instance, according to the Austrian Report on the Philadelphia Expedition (1876), proper receivers cannot be obtained at all, and have had to be brought from the Aussig Chemical Works in Bohemia, notwithstanding the enormous cost of transit. Good

stoneware receivers &c. are, besides, supplied in England by the Lambeth potteries, in France by the Beauvais potteries, in Germany by those at Zwickau and Charlottenburg, near Berlin. The shape usual in Germany is shown in fig. 112, the English one in fig. 111. Decidedly the best shape in a constructive point of view is that made at Aussig (fig. 113, p. 210). The bottles are about 3 feet 3 inches high; the bellied continental shape is in the centre from 2 feet 2 inches to 2 feet 8 inches wide, the cylindrical English shape about 2 feet wide. They hold from 36 to 38 gallons.

Fig. 111.

Fig. 112.

Most German factories get their receivers and other stoneware

apparatus from the Aussig Chemical Works, whose general manager, Mr. Schaffner, has established works for that purpose, where more care is devoted to the preparation and moulding of the clay (from Bilin, near Aussig) than perhaps anywhere else, and where both labour and fuel are very cheap. A new kind of moulding has been introduced there—viz., instead of on the potter's wheel, the receivers &c. are moulded in plaster-of-Paris shapes from clay slabs cut off by a wire from a block: thus they become very accurate and neat, nor can the best eye discover the original joints, which on burning would become wider, of course. The Aussig receivers have indeed an excellent reputation for their resistance to acids and to changes of temperature.

The two upper wide necks serve for receiving the siphon-shaped connecting pipes, in which the gas is carried in and out; they are from 6 to 8 inches wide. The middle neck, usually stoppered, serves for pouring in water; it is 2 inches wide, as well as the lower one, into which a stoneware cock of ½ to ¾ inch bore is ground in. The latter is not required if side branches are present through which each bottle is connected with its neighbours; only the last of them in that case needs a cock. There is no difficulty in grinding in the cocks so that they close perfectly tight; but in consequence of bad work they frequently leak at the joint. It is not easy to mend matters by cement, as there is no chance of stemming any in, as can be done in tanks made of stone flags. The acid can also be drawn off without any cock by a siphon put into the upper neck. Such siphons are made of gutta-percha and stand a long time, as faulty places can be easily mended by cutting a piece out and putting another one in. Gutta-percha can be soldered perfectly by means of a hot iron.

The receivers are always combined in series such as have been figured on p. 48, in describing the older sulphate-furnaces. Usually there are two rows for each pan, and as many for each muffle; two rows are employed, because the connecting pipes cannot easily be made wide enough to afford sufficient draught with a single one. They are made of the same mass as the bottles themselves, and a little narrower than the necks, but provided with a flange or a conically widened out end (fig. 112), lest they should go down too low. Often they are made pretty high, say 3 feet, in order to cool the gas. The pipes are cemented into the bottle-necks with the same cement that plays such an important part in the condensation

of muriatic acid, and which has been frequently mentioned above. It is made by well kneading-up thickened coal-tar with as much finely ground china-clay or pipe-clay as it will take up, and well beating the mixture with wooden mallets till it has become a perfectly homogeneous plastic mass, which is moulded into brick-like blocks, and can be kept for some time. It is called at the works "black stuff," sometimes (in Lancashire) "barytes." In larger quantities (for instance, if a whole condensing plant has to be built) this cement is made in the cheapest and best way by grinding up the ingredients under edge-rollers, for instance in a chalk-mill. Before use it is moderately warmed up and stemmed into the joints by means of bits of iron. It gives very tight, acid-proof joints, and in time becomes harder when heated, of course not up to a red heat. Where it cannot be stemmed in, it must be used in a softer state; but it then does not make such strong joints.

A less resisting, but more elastic cement is obtained by melting up coal-tar with some rosin, and kneading it with finely ground pipe-clay and sand.

Sometimes the receivers are connected by water-lutes, as will be shown later on (fig. 113): in this case the pipes are not so firmly fixed, but they can be very quickly put in and taken out if need be.

The first receivers of each row are always connected by a forked stoneware pipe with the gas-pipe of the pan or muffle, unless, as at Aussig, the gas first passes through a small tower in which most of the sulphuric acid is condensed by injected water, and the gas is so much cooled that the first receivers are much less subject to cracking. The last pipes go into a chimney, or (which is much better) into a coke-tower (see below).

If each bottle is filled and emptied by itself, the whole series stands on the same level; the acid gases are nearly deprived of their hydrochloric acid and other constituents soluble in water already in the first few bottles; and in these a strong acid is formed, showing in winter 34°–36° Tw., in summer 28°–30° Tw.—the latter partly because acid of equal percentage of HCl at a higher temperature occupies a larger volume, partly because in warm weather it is not at all possible to make such a strong acid, owing to the decreasing solubility of HCl in water with increasing temperature. The later bottles of the series then serve for absorbing the small quantities of HCl which have escaped condensation in the first

bottles; and only very weak acid is formed in them. Whilst, therefore, the first bottles can be daily emptied and refilled with water, and yet furnish strong acid, the later bottles not only have to stand much longer, but they cannot wait till their acid has got up to strength, since in that case much HCl would escape condensation. Their contents must therefore be regularly withdrawn in the state of weak acid and filled into the first bottles, in order to get up to strength therein, whilst fresh water is put into the last bottles.

This process requires much labour; and on emptying and refilling the bottles the draught in the decomposing-pans and furnaces is very much interfered with; thus much acid vapour escapes from these and from the open necks of the bottles. All the best factories therefore now work differently. Usually the bottles are placed terrace-fashion on an inclined plane, only the top bottle is fed with water, and acid is only withdrawn from the bottom bottle. The current of acid gas travels in an opposite direction, first into the strongest bottle, whose contents it entirely saturates, then over acid less and less concentrated, and ultimately over pure water. This is evidently a rational arrangement. Without any manual labour water is continuously run in at one end and strong acid is run out at the other end. But if the acid has at once to be filled into carboys, the labour required for this has to be furnished. Some arrangement must in this case exist for the liquid to flow out of each bottle into the next lower one. But it is much better if the bottles are combined in such a way that the acid lying on the *bottom* of the higher bottle, being a little heavier and more concentrated than that on the top, runs into the next lower bottle. The way in which this is done will be shown very clearly later on, in describing the Aussig apparatus. One of the two side openings (fig. 113) is connected with a moulded-in stoneware pipe, which goes almost down to the bottom of the bottle, and causes the outflow always to begin from there. The connexion between two bottles is made by short glass tubes, which are joined to the thickened edges of the side branches by strong elastic tubing; or the side branches are moulded so as to bend upwards, and are joined by small glass siphons reaching from one bottle to the other. The simplest plan is to put into the side openings india-rubber corks, through which a short glass connecting tube passes.

It is sufficient to place each following bottle 1 inch below the preceding one; so that a whole series requires only about 3 feet fall.

Fig. 113.

Sometimes, in order to cool the gases better, the receivers are placed in a tarred wooden trough into which cold water runs at one end; this, however, is not easily combined with the terrace arrangement just described. In this case it is still possible to run water upon them from the outside, but at a considerable risk of cracking them. At all events the bottles ought to be protected against the direct action of the sun by a light roof.

The following arrangement permits working with ordinary Woulfe's bottles without side branches, and yet of attaining to a great extent the advantage of systematical condensation and saving of labour. There are two rows of bottles, as usual. The gas, however, only travels through one of them, A, in one direction, and returns in the other, B. Next day the pipe-connexions are changed, and the gas is first admitted into B, *i. e.* into that bottle which on the preceding day had been the last of all; and it then returns through the series A, which has now been filled with fresh water. This change is made every day. All the bottles of one series are filled and emptied at a time. They have each a neck at the bottom; over this a gutta-percha tube is put, which joins a main pipe running along the whole series; the latter lies in a wooden shoot, to prevent its sagging by heat; and its projecting end is ordinarily bent upwards. Thus all the bottles are connected with each other and with the main pipe. At the end of the shift,

when that series of bottles has had the gas twice, and consequently contains strong acid, this is emptied out of all the bottles at a time by bending downwards the projecting end of the main pipe; then the latter is bent upwards again; and now, if water is run into any one of the bottles, all of them are getting filled at the same time.

For condensing the pan-gas not quite so many receivers are needed as for the muffle-gas, because the former is richer in HCl and comparatively cool and moist. From 35 to 50 bottles suffice for an ordinary small pan, decomposing daily from a ton to 30 cwt. of salt. The much more dilute, hotter, and drier furnace-gases are more difficult to condense, and there ought to be 70 or 80 bottles for each muffle; and even then the gas cannot be condensed very well by these alone, nor can any very strong acid be obtained from it. Sometimes, on the contrary, a larger number of receivers are employed for the pan than for the muffle. In order to fix the last portions of the acid, which in receivers are not retained by mere water, Kuhlmann employed *milk of lime*, poured over cokes in a special apparatus, and thus offering a large surface to the current of gas*. He did this in stoneware bottles also, but with a very large mouth, closed by a lid and a water lute, to which at the same time a funnel for running the milk of lime was attached. The vessel is filled through the mouth with lumps of coke of the size of a fist; the liquid runs about halfway up the bottle; the upper half of the latter is therefore filled with coke alone and exposed to the gas. The milk of lime, continually running in from a higher reservoir, runs off below as calcium chloride. The pan-gas of a furnace decomposing 266 kilog. salt with 279 kilog. sulphuric acid of 58°-60° Baumé (in what length of time?) first passes through 66 ordinary bottles, then through 6 lime-bottles of the sort just described—that of the roaster through 36 ordinary bottles, then through 4 lime-bottles, and ultimately through a flue filled with quicklime, several metres long, before they get into the chimney.

This process, employed for some time at Kuhlmann's works, is not at all to be recommended; and it is inconceivable how, so long after the introduction of Gossage's coke-towers, it could have been

* Kuhlmann is usually quoted as the inventor of the following apparatus, which certainly was first (and perhaps exclusively) at work in his factories; it was not he, however, but Marsilly, who proposed this arrangement, when the inhabitants of Amiens complained of the vapours escaping from Kuhlmann's works; and the latter was compelled by the authorities to adopt it. (Annales des Mines, vi. (5) p. 100.)

P 2

invented, and even commended by some. The whole arrangement is very complicated, exposed to constant disturbances, can only act imperfectly (on account of the low fall of the milk of lime), and involves the loss of all the lime. The Belgian Commission (comp. p. 68 of their Report) carefully investigated this plan, and rejected it as quite useless. Even when the lime was constantly stirred up, which on the large scale would not be practicable in this apparatus, a large quantity of uncondensed HCl passed through; and the Belgian factories consequently found themselves compelled to give up the process again. Afterwards Kuhlmann himself replaced the lime by natural barium carbonate, in order to utilize the barium chloride for the manufacture of permanent white ($BaSO_4$). At his factory at Roche-lès-Amiens there are for each decomposing-furnace 160 receivers, 30 of which contain barium carbonate; ultimately the gases enter a mechanical washer, viz. a cistern covered with a wooden lid, in which an agitator causes a continuous spray of water, holding finely ground barium carbonate in suspension. From 100 parts of 92-per-cent. salt, along with 140 parts hydrochloric acid of 34°–36° Tw., another 20 parts of acid combined with baryta are said to be obtained. Even this second method (which, according to Stas's report, affords almost perfect condensation) is not recommended from a technical point of view; it is tied to a material obtainable only in restricted quantities, and produces a by-product only saleable to a very limited extent; moreover it is much simpler and cheaper to decompose the barium carbonate, without grinding it finely, in special apparatus by means of the dilute acid which might be obtained by a coke-tower placed behind the receivers. It is not even necessary to make any weak acid at all: all the water can be run onto the tower, and from this into the first receiver, so as to be ultimately discharged as strong acid.

Another half-measure, and consequently unsuitable, is the use of the "cascade-bottles," sometimes placed at the end of the series, provided with a wide central opening, in which a perforated funnel fitted with coke is introduced, and water run down the same; for of course the gas does not pass *through* the funnel, but only *round* it, and the whole complicated arrangement does very little good.

It may be assumed that for each 100 kilog. salt 140 to 146 litres of water must be run through the receivers, if strong acid is made exclusively; in practice, where much weak acid is made in the last washing of the gas, perhaps twice as much water is used.

Condensation by receivers alone is only suitable for small or

medium-sized works, especially if strong and pure acid is aimed at; even then it can be replaced by a combination of stone tanks and coke-towers. For the same quantity of salt decomposed, receivers in large works are sometimes more costly than coke-towers; they require much more space and supervision, and are often very troublesome through frequent breakages of bottles. This holds good less of pan-receivers than of muffle-receivers; every thing of course depends upon the quality of the ware. Long series of receivers very much check the draught, without affording a sufficient equivalent for it, as coke-towers do, where the increased friction goes hand in hand with an increase of condensing-surface. The advantage of better cooling, which receivers have against the larger stone tanks, is counterbalanced by the multiplication of apparatus and of joints.

The principal drawback of receivers, when employed by *themselves* (and not merely as introductory to coke-towers), is that the liquid and the gas have comparatively few points of contact with each other. If on cementing the arms in the bottle-necks a little tar cement has got inside, the thin oily layer forming on the liquid prevents that contact completely, and the bottle in question ceases to work: this can be ascertained by its remaining cold. Receivers by themselves consequently are not to be recommended; but combined with coke-towers of considerable size and made of the very best material, as in the Aussig system to be described hereafter, they are adapted for all but the very largest works, in which, in the English fashion, each pan is intended to accomplish its maximum of work.

The most important advance in the condensation of hydrochloric acid was the introduction of the previously mentioned *coke-towers*, invented by Gossage in 1836, *i. e.* tower- or column-shaped apparatus of stone, brickwork, or stoneware, filled with coke or some other porous material, over which a continuous rain of water trickles down, whilst the gas from which the HCl is to be removed passes likewise through the tower, and that best in an upward direction—that is, opposite to the current of water. Gossage himself, as can be seen from his 'History of the Soda-Manufacture,' p. 27, derived no pecuniary advantage from the general adoption of his invention, but, on the contrary, suffered the loss caused by the first costly experiments.

It is well known that coke-towers are now the principal condensing-apparatus in nearly all the larger alkali-works. Their

action is based upon the following facts (very clearly pointed out by Dr. A. Smith). When the air contains but very little HCl (say 0·003 per cent.), it already appears cloudy in damp weather. Even when it has been condensed in a rapid current through well-cooled pipes, it still appears cloudy on leaving them; but when it has been passed through small pieces of coke or through very narrow damp channels, it issues clear. The floating acid particles which are too small to be precipitated seem to be retained like precipitates on a paper filter. The essential point is therefore the surface-contact; and few materials offer such a large outer and inner surface as coke. Its inner surface, enormous as it is, is not directly utilized, since the pores are filled with liquid acid and do not allow the gas to pass: stones or bricks would therefore seem to afford the same action; but the pores of coke act indirectly by the continuous diffusion of acid from within and fresh water from without. Some factories, indeed, employ fire-bricks or specially moulded fire-clay lumps with many perforations (see below). Sometimes with open roasters bricks are employed in the lower and coke in the upper part of the condensers. Still, for the sake of simplicity, we sometimes call all these apparatus "coke-towers" or, generally, "condensers." The object of employing bricks is partly to afford wider spaces in cases where any soot might be deposited, partly to avoid ignition of the coke by hot gases from open driers.

Coke-towers are nearly always of square section, occupying 9 to 64 square feet of ground-space, and 5 to 120 feet high. They are employed either single or several together; they communicate either with the open air or with a chimney. Of course these conditions are not arbitrary, but are determined by circumstances, such as the size of the batches, the kind of roaster, &c. But as the gas always issues very hot, especially from the roasters, cooling it by long conduits is of great advantage; otherwise the condensers themselves get very hot. If this is sought to be remedied by running down very much water, a dilute acid is obtained, and the passage of the gas may even be obstructed too much.

The furnace-gases cannot be completely condensed in a single tower, if strong acid is to be made; but the gas is allowed to pass through a flushing-tower or post condenser, where it is washed with a good deal of water, whilst the resulting very weak acid is run to waste, unless it is pumped up for feeding the proper condenser. The pan-gas by itself can be condensed by a single tall coke-tower not connected with a chimney.

Condensers, according to Dr. A. Smith, may have the following defects. If the coke is too loosely packed or the pieces are too large, there is not enough surface opposed to the gas; the layers easily collapse, form compact masses, and allow the gas to pass more easily through another part of the sectional area. In this case a large portion of the tower remains inactive; and consequently the really efficient portion of some very large condensers is very small. Exactly the same thing happens when the coke is packed too tightly. In this case so much resistance is offered to the gas that it seeks the opener passages, never totally absent. A very bad case is that of condensers getting out of plumb. Then the water does not run down equally, and the gas of course principally ascends on the dry side, where it meets with less resistance. Thus a large tower, fed with much water, may become worthless, as actually happened in a Tyneside works. There this was partly remedied by putting in wooden shelves on the overhanging side, which compelled the water to flow across to the other side of the tower. Very frequently the condensers are too small. This can be counterbalanced by a larger feed of water, but only to a certain degree. A certain time is required for condensation; and if the condensers are not high enough, the largest supply of water cannot make up for this. A large condenser consequently always works better than a small one. Cases have occurred where a strong current of water ran down and arrived only faintly acid at the bottom, whilst the gas escaped strongly acid at the top. If too much water runs down, the surface of the coke is even lessened and its efficiency impaired. The arrangements for dividing the water before it runs onto the coke are also often very imperfect. It is very important that the gas should always travel in the opposite direction to the water—that is, always upwards. Condensers with an internal partition, in which the gas first goes upwards in one compartment and downward in the other, are faulty. The first Report of the Inspector on the Alkali Act mentions a very telling case, in which such an inefficient condenser was at once cured when the gas was taken from the top downwards by a string of pipes and made to ascend in the second compartment as well.

The draught through the condensers should not be too strong; if the gas is pulled through too fast, condensation cannot be perfect. This does not easily happen with condensers open at the top, which, however, can only be used for pan-acid. For condensing the roaster-acid, or both together, especially for open roasters,

more draught is required, and the condensers must be connected with a high chimney. At a Tyneside works the condensers situated nearest to the chimney, and exposed to the strongest draught, condensed much worse than those more distant. Suitable dampers ought to be sufficient for correcting this fault.

The efficiency of condensers is much promoted by a previous cooling of the gases. Good condensation may be assumed to take place if there is a difference of temperature of 50° C. between the gas entering and that leaving the towers. The more the gases are previously cooled, the less work the condensers have to do, and condensation is all the more perfect. In a rational condensing-apparatus the gas must always pass through a channel where it can be cooled by the outer air; this is best done by pipes of different material, either by themselves or in connexion with stone tanks offering a large surface. In some places there are large brick chambers (not filled with coke) for the same purpose. The stoneware receivers, if employed in this way (that is, in connexion with a coke-tower), also act very well indeed.

The most natural occasion for cooling by pipes occurs when the decomposing-furnaces are at some distance from the condensers; sometimes they are purposely laid out in this way up to 300 feet away from the towers; or, if the space does not admit of a long horizontal conduit, the gas is sometimes first taken upwards, say 50 feet, and then downwards again, before entering the condensers. (Compare later on.)

Some direct experiments on the cooling action of earthenware pipes are described in the Third Report on the Alkali Act, p. 40. At Kurtz's works, at St. Helen's, the pan- and furnace-gas together pass through a 12-inch pipe. Just behind the furnace the temperature was 170° C.; 6 feet 3 inches further on, 136½°; and 7 feet 3 inches further on, 110° C.: thus in a length of 13 feet 6 inches it had been lowered by 60° C. (that is, 4°·44 C. per foot of its course). Now the gas entered into a stone tank of a capacity of 200 cubic feet, and left it with a temperature of 76°·5; after a further passage through 18 feet of 12-inch pipe its heat was 60° C.; the condensation in the coke tower was perfect. It is true that the outer temperature during the experiment was only 6° C.

At another works the temperature of the gas after passing through 94 feet of earthenware pipe sank from 162° to 75½° C.; and already after the first 40 feet it had got down to 86°·5. In a third works, also perfectly condensing its HCl, the gas just behind the

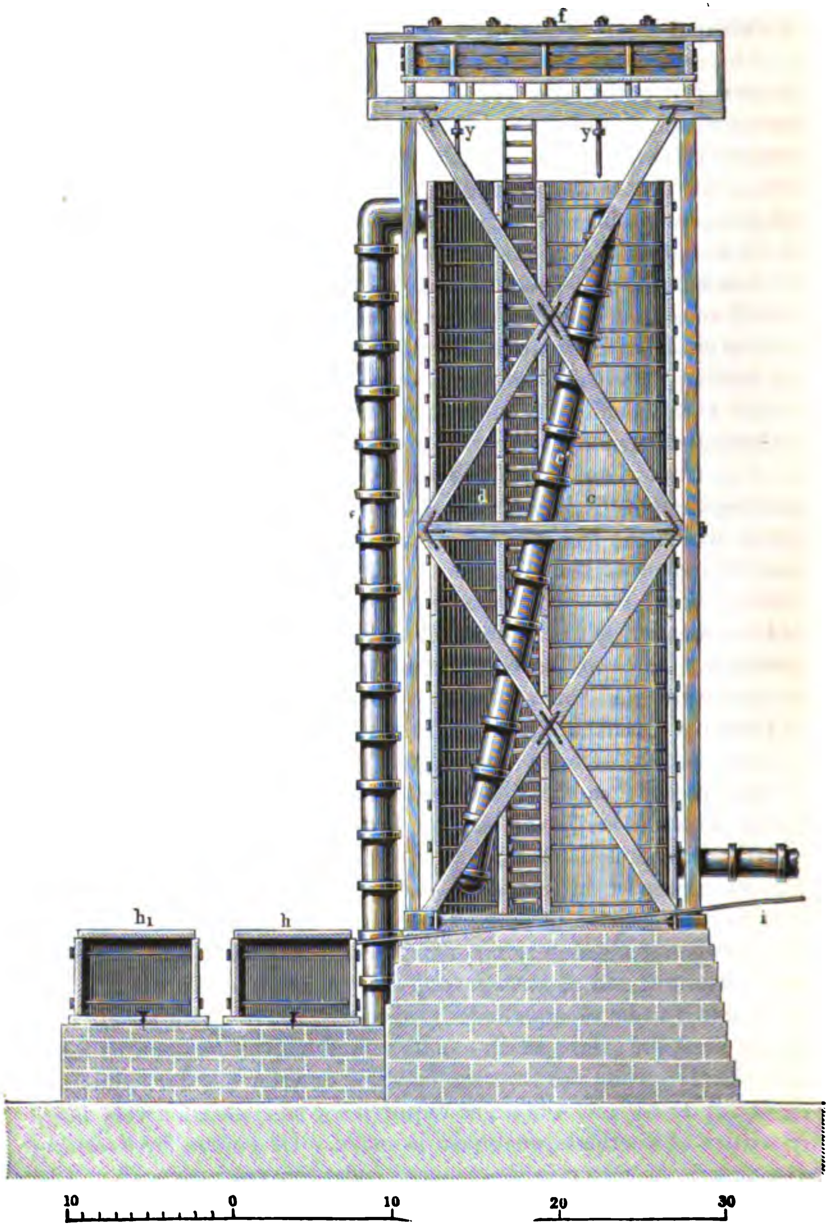
pan showed 123° to 149°, and after passing through 250 feet of piping, 34° to 41 C°.

Very instructive are some observations on the cooling influence of different kinds of gas-flues contained in the fourth Report, p. 53. All three flues belonged to open roasters. The first was an *underground brick flue,* 160 feet long, of 1600 cubic feet cooling-space. Temperature on entering about 360°; on leaving, 300° C.; that is, a cooling of nearly 4° C. for each 10 feet length, or of 10° C. for each 261 cubic feet. The second was an *overhead brick flue,* 160 feet long, and containing 1300 cubic feet cooling-space. Temperature on entering, 360° C.; on leaving, 88° C.; cooling 17° C. for each 10 feet length, or 10° C. for each 47·7 cubic feet. The third consisted of *cast-iron pipes,* 2 feet 3 inches wide and 130 feet long, of a capacity of 518 cubic feet. Temperature on entering, 360°; on leaving, 138° C.; cooling about 17°·1 C. for each 10 feet length, or 10° C. for each 23·2 cubic feet. In later Reports we find the following statement for cast-iron pipes: length of piping 124 feet, cooling from about 360° C. to 138° C.; length of piping 105 feet, cooling from 470° (pyrometrical measurement) to 138° C. *Glass* pipes, which can hardly compete with the materials just mentioned, will be spoken of later on.

A proposal for further cooling the gas, made by J. Mather, is communicated by Dr. A. Smith, who himself is not very hopeful about it. Air is to be compressed, cooled down to the ordinary temperature, and introduced into the gas, which it is to cool on expanding. It is well known that the generation of cold by the expansion of previously compressed and cooled air is not at all a cheap process; and in this case the condensation is certainly rendered as much more difficult by dilution with air as it has been aided by cooling. A sketch of his apparatus is found in the Eleventh Report on the Alkali Act, p. 39.

The interposition of stone tanks between the furnaces and condensers is not absolutely necessary; even without them, complete condensation, and of strong acid, can be attained. Still they are very much to be recommended, especially where much strong acid is required for sale. With condensers alone the acid can be made sufficiently strong for own use (say 28° or even 30° Tw.), but not easily up to 34° or 36° Tw., as required for sale, unless a very large quantity of worthless weak acid is made. Of course by lessening the supply of water in the proper condenser, stronger acid will be got; but then more gas will pass over into the post condenser,

Fig. 114.

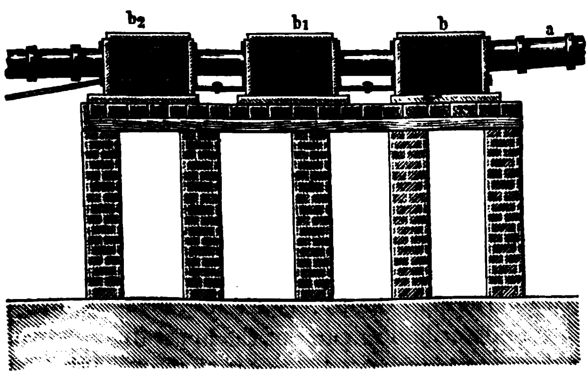


where it has to be condensed into weak acid. Practice has shown that with properly constructed condensers *without* stone tanks the acid need not be below 28° Tw.; but it cannot well be made stronger without incurring the inconvenience just mentioned.

The number of stone tanks may be assumed to be three, which is sufficient for most purposes. In the first of these most of the sulphuric acid carried along with the HCl is condensed; the acid contained in this tank is consequently very pure, and that of the two following ones all the purer. This, however, only holds good of pan-acid; roaster-acid can never be obtained free from sulphuric acid, because it is partly present in the furnace-gas as anhydride, which is very difficult to condense completely. When there are several tanks they can be connected, and a stream of water or dilute acid may be run in them in the direction opposite to that of the current of gas, just as is done in the stoneware receivers; but the tanks are simpler, last longer, and the gas-pipes can be made much larger than with Woulfe's bottles.

Fig. 114 is a sketch of a condensing-plant sufficient for the complete condensation of the gas from two English blind roasters producing 80 tons of sulphate per week. At *a* are the pipes conveying the gas from the furnaces; they must rise high enough above them to have a fall of ½ inch to the foot down to the first tank *b*. The gas issues from the furnaces in 15-inch pipes, which either enter separately into the cistern *b*, or are united beforehand by a Y-pipe; the common pipe carrying them onward should have 21 inches diameter.

Fig. 114 (*cont.*).



It is preferable to introduce the two 15-inch pipes separately, because one of them can easily be stopped when either of the furnaces has to stand still for repairs. The three stone cisterns b, b_1, and b_2 are connected at the bottom by 1- or 2-inch stoneware pipes; and each of them is provided with an outlet-cock. The pipe i connects them with the stock-cisterns h and h_1, and allows either all the acid condensed in b, b_1, and b_2 to run into them, or perhaps only that of b, for bleaching-powder-making, whilst the purer acid from b_1 and b_2 can be drawn off into carboys for sale.

The tanks should be placed so that the gas will rise from them to the first coke-tower—best of all, so low that the tower-acid can run into them; but there should be a fall to the store-tanks as well. The latter case is not provided for in the drawing, which of course must be modified in each factory according to the given conditions of level. The gas then enters a coke-tower, c, 7 feet square and 45 feet high; from this it is taken down in the 21-inch pipes c', and enters the post condenser d, which is also 45 feet high, but only 4 feet square. From this it issues at the top and descends through e downwards into a flue leading to the chimney. In this there must be a suitable damper, made of slate or rough plate glass &c., and never opened wider than is absolutely necessary.

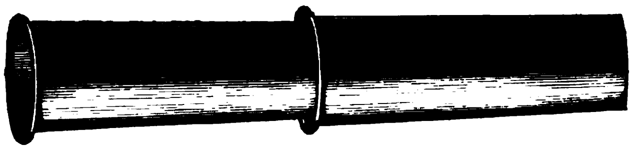
It would be of course much simpler to connect the towers c and d at the top; the gas would then ascend through c and descend through d; the two strings of pipes c' and e would thus be saved. But this saving amounts to very little in comparison with the much more perfect condensing effect of the arrangement as first described.

The two towers are fed with water from the wooden cistern f, which is fixed on a scaffold over the towers; so that there is space for a man to stand between the top of the tower and the bottom of the cisterns. The cocks y y supply the water, in a manner to be described in detail later on.

The condensed acid is run from c into the cisterns h h_1, of which one is always filling whilst the contents of the other are getting used in the chlorine stills &c. These cisterns ought to be placed high enough for the acid to run to the stills by itself; only in the most urgent cases ought pumping of hydrochloric acid to be resorted to (see below). It is still better to make the condenser-foundations high enough for running the tower-acid into the tanks b, b_1, and b_2.

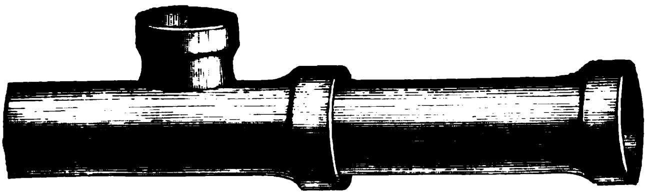
We shall now describe the parts of the apparatus separately, and begin with the *pipes* conveying the gas away from the decomposing-furnaces.

Fig. 115.



Formerly these were always made of a tapering shape, one pipe projecting into another, with the cement stemmed in between them (see fig. 115). The amount of the tapering is such that pipes of 4 feet 6 inches length are 15 inches wide at one end and 18 inches at the other. Such pipes can only be made by hand, and are consequently dear. Many manufacturers therefore choose the shape fig. 116, which is much more easily and cheaply made. The joints

Fig. 116.



are made good by the above-described tar and china-clay cement. Linseed oil and red lead is also sometimes employed, but it is much dearer and not so suitable.

As far as the size of the pipes is concerned, a 15-inch pipe will do for both pan- and roaster-gas of a blind roaster producing 40 tons per week. Some factories only make them 12 inches wide; but 15 inches is preferable, on account of taking the gas away more quickly. A 21-inch pipe is sufficient for the gas of two pans and two blind roasters. The single pipes are made as long as practicable, so as to have fewer joints. It need hardly be said that the pipes must be supported in such a way as to enable the joints to be made good all round, and that the sockets of the pipes should be at the highest point if there is any fall.

The usual material of the pipes conveying hydrochloric acid vapour is stoneware or fireclay. It is not easy to get pipes resisting both the changes of temperature and the acid gases. This, however, is the makers' fault; for good pipes can be made without any special difficulty, only with sufficient care, as is proved by the Tyne Chemical Works at Gateshead-on-Tyne (formerly Messrs.

Allhusen and Sons), who make their own pipes, and to whom their neighbours readily pay *twice* the price asked by ordinary pipe-makers. Their pipes are made of fireclay by hand, without glazing, and previously to use are boiled in tar for at least two days. Most other pipes are machine-pressed. They are always best left unglazed and boiled in tar, because they then resist better both acids and cracking than glazed pipes, which cannot be boiled in tar; but even the tar-boiled pipes frequently crack. In Lancashire sometimes pipes made of ordinary stoneware, "sanitary" pipes, are employed. The Aussig ware has been mentioned already. The best, but dearest, pipes are those made by Messrs. Doulton and Watts, of Lambeth, of very carefully prepared stoneware. They are much thinner and longer than ordinary pipes and cool the gas very well; they also stand very well. For some time glass pipes were in much favour in many Lancashire works; their introduction is due to Mr. Alfred Fletcher. Owing to their thin walls, they cool the gas very well indeed, and do not easily crack, especially if protected from rain and snow by a shelter. They are always made a little tapering; and the thinner end of one is put into the thicker end of another. They can only leak at the joints, if badly cemented, like *all* pipes; but they are perfectly air-tight in their body; whilst earthenware pipes frequently allow the gas to escape all over, or even liquid to ooze out. The latter occurs with Lancashire stoneware pipes much more than with porous fireclay pipes boiled in tar. Glass pipes are as cheap as stoneware pipes. Their cooling action, in a string of 300 feet length, was found to reduce the temperature from 155° C. at one end to 57° C. at the other end, with an outer temperature of 7°. If a fine jet of water is allowed to enter at the hotter end, up to two thirds of the acid condenses already in these pipes. They are not only employed for pan-gas, but also for blind roasters, and, if properly supported, stand better than any earthenware pipes. Quite recently glass pipes have gone out of favour again; the reason alleged is that the glass-works no longer supply them of the same quality as before; they have been found in the end most suitable for cooling the gas in Deacon's chlorine-process, where the gas within them is under less pressure than the air without.

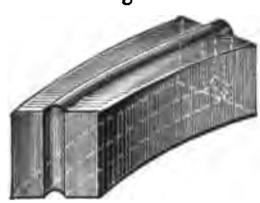
It is a very common practice to employ some of the pipes cut through lengthways, so that the upper half can be taken off; of course, for use, the two halves are cemented together. If one such

pipe is put in about every three yards, the cleaning of the series from the accumulating deposit is much facilitated.

The whole series of pipes, both for pan and roasters, is always arranged in such a manner that it is first taken straight up to a sufficient height for getting afterwards a continuous fall towards the first tank or receiver, or, in the absence of these, towards the condenser itself. This is done to prevent the running back of any condensed acid.

Even with blind roasters, as we have seen, it is preferable to employ separate pipes for pan and roaster; for open roasters this is absolutely necessary. With these the employment of earthenware pipes immediately behind the furnace is not advisable, owing to the great heat; either brick flues or cast-iron pipes are preferred. *Brick flues* are sometimes carried underground, but not at all advantageously; for although with the hotter open-roaster gas condensation of liquid acid and destruction of the flue does not take place as readily as with blind-roaster gas, yet in long flues this may happen after all, and large quantities of acid may sink into the ground before it is perceived. Moreover those underground flues do not fulfil one of the principal functions of condensation, viz. good cooling, as we have seen above. Better service is afforded, but only for the vertically ascending part of the gas-flue, by flues made of specially moulded fire-bricks, as shown in fig. 117. They are shaped to the sweep of the flue, and provided with feather and groove; if very fine tar-and-pipeclay cement be put into the joints, the flue will be very tight and stand well without repairs.

Fig. 117.



At the larger English works latterly *cast-iron pipes* have mostly been employed for conveying the furnace-gas from open roasters. Of their cooling action we have treated on p. 217. They may be employed without any danger of being destroyed by acid so long as the gases are hot; and just their excellent cooling action is their greatest recommendation. But as soon as the current of gas has cooled down so far that liquid acid might be condensed, say to 100° or 120° C., the metal pipes must be discontinued, and the further conveyance of the gas must take place through earthenware pipes. With the assistance of metal pipes, stone tanks may be employed even for open-roaster gas,

which otherwise would crack them too easily. The actual length for which metal pipes may be employed without danger of too much cooling and subsequent corrosion depends entirely upon the style of work in the furnace. The more salt is decomposed in a certain time, the longer the current of gas will remain hot enough for metal pipes. Usually 60 to 100 feet of metal piping form the limit which must not be exceeded; but occasionally the length may reach 300 feet.

The metal pipes are usually cast in lengths of 9 feet, and 2 feet to 2½ feet wide; they need not be above 1 inch thick. They are either cast with a socket at one end, into which the other end fits, or with straight ends, over which a loose ferrule is slid and cemented on both sides with tar and china-clay. If the pipes have to be cleaned out, the cement is softened by heating, the ferrules are slid sideways, and the pipe is lifted by means of a winch, so that both itself and its neighbours become accessible inside.

There is always some deposit formed in the iron pipes; but the amount varies much: it is sometimes so great that they have to be cleaned out once a week, sometimes so little that cleaning them out once a year is sufficient. The following analyses (from the Alkali-Act Reports) show that this deposit consists of sulphate carried along by the gas, together with the products of the action of sulphuric acid upon the iron, this acid being precipitated in a liquid form long before the HCl.

Ferric oxide	19·866	26·946	6·400	19·483	27·407
Alumina	3·171	4·614	3·545	3·905	4·689
Lime	0·371	0·486	2·110	1·383	0·482
Magnesia	0·414	0·298	0·751	0·708	0·281
Soda	11·311	2·808	24·093	12·653	6·003
Silica	6·049	3·309	13·020	3·292	4·166
Sulphuric acid (SO_3)	53·212	48·077	48·695	54·286	26·220
Chlorine	2·141	2·034	0·092	2·278	20·409

Flues made of stone flags are also employed for roaster-gas; the stone should not only be able to resist the acids, but also the changes of temperature. It is a very good arrangement to give the flue a little rise towards the coke-tower, and to allow the acid of the latter to flow down the bottom of the flue; this unites all the advantages of acid-tanks with thorough cooling. At the other end of the flue the acid is got as strong as pan-acid, but, of course, less pure. The sketch, fig. 118, will make this clearer. The upper arrows show the path of the gas, the lower arrows that of the liquid.

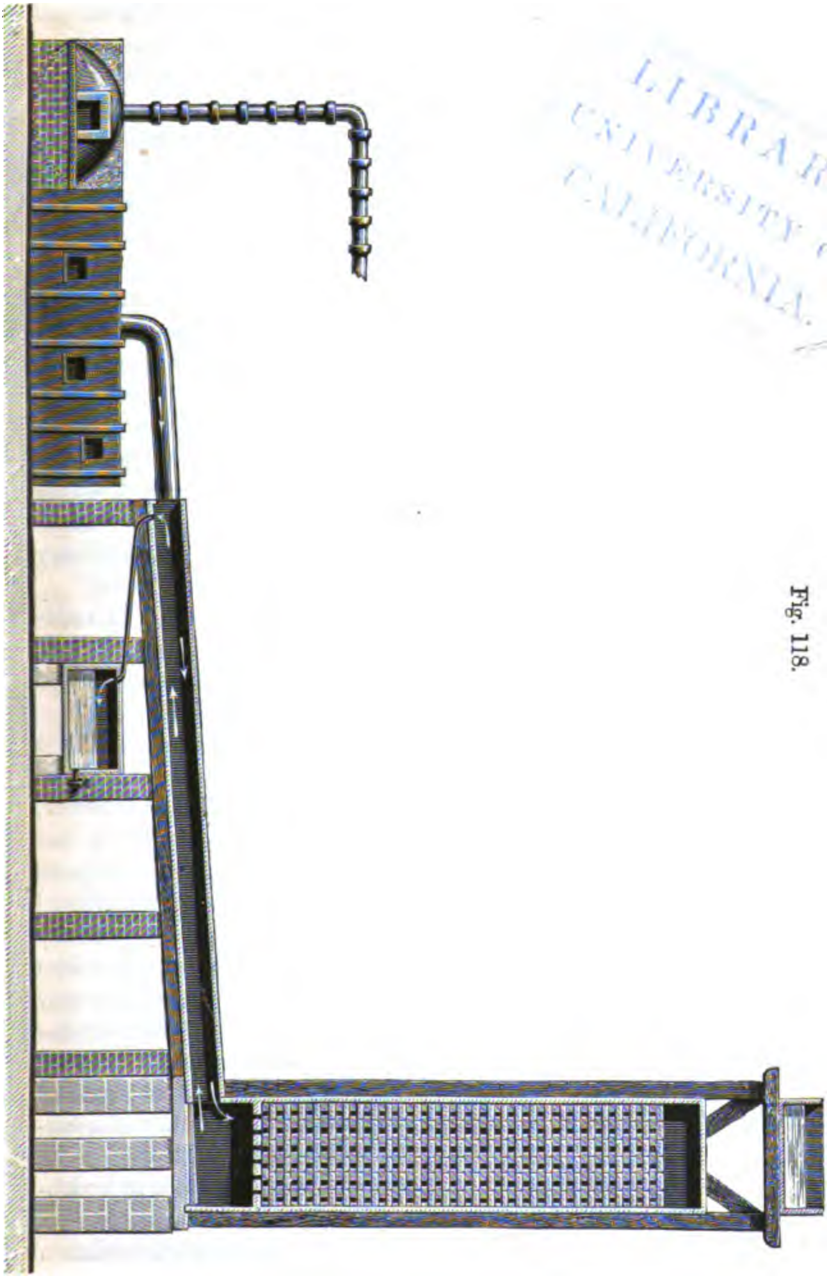


Fig. 118.

Circular flues, made of two semicylindrically hollowed blocks of stone, are used at some German works with great success.

If (from local causes) the condensers are considerably less than 100 feet away from the furnaces, the necessary length of pipes for cooling is managed in this way: they are first carried a little downwards so as to prevent condensed acid from running back into the pan; then they are carried upwards for, say, 50 feet, and down again, and ultimately into the condenser. In the lower elbow there must be a hydraulic lute for the condensed acid, which is very impure. This arrangement is met with both for pan- and roaster-gas, with earthenware, iron, stone, or brick flues. It is also employed for Newall and Bowman's water-spray process (see p. 203). On the largest scale this multiplication of cooling-surface is found employed for the very hot gas from Hargreaves's sulphate process, where the pipes are not only carried a great length, but are also multiplied by admitting the gas into a long trough, from which a number of parallel strings of pipes convey it into another, similar trough, communicating with the condensers. Even for ordinary sulphate-gas such an arrangement is met with here and there.

Sometimes, but rarely, the gas-pipes have been placed in cold-water troughs; in such a trough of 24 feet length the gas was cooled from 250° to 180° C. This takes much water, and cannot compete with air-cooling in cheapness.

As far as the *coke-towers* themselves are concerned, the first thing to be considered is the *foundation*. This can hardly be constructed too carefully—not merely because the weight of the tower, with its packing and the water-cistern, is very considerable, but also because the running-over of acid, which cannot possibly be absolutely and at all times prevented, tends to make the ground all round and the material of the foundation itself rotten, especially the mortar. Unless it is possible to go down to the rock, a firm building-ground must be procured by piling, just in the same way as for a very high factory-chimney. On the bottom of the foundation-pit first a layer of asphalt is laid, either the same kind as is used for street-pavements or a mixture of boiled-down coal-tar and sand. Upon this the foundation proper is erected, either of quarried rubble stones, or, preferably, of hewn freestone. Either stone must be free from limestone or any other mineral soluble in hydrochloric acid. Most suitable is sandstone with siliceous cement. When freestone is used, it is not necessary to build the foundation

as a solid block, but merely three strong pillars, especially that part of it which projects out of the ground, and which must be carried high enough for the acid to have a natural fall to the tanks and thence to the chlorine-stills. Supposing the latter to be Weldon stills (*i. e.* about 12 feet high all over) and the building-ground to be quite level, the height of the foundation from the ground to the condenser-bottom will be at least 18 feet; 20 feet will be better.

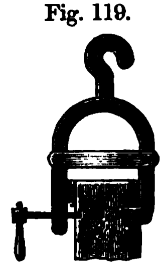
The mortar, even for the foundation, ought not to be either lime or Portland cement, but tar and sand. At the ground-level another layer of asphalt is laid down, which slopes away from the centre in all directions, so that no acid can lodge in any one place; a gutter is provided for taking away any acid running over, as well as the rain-water.

Upon the foundation is placed the timber frame which has to support the stone erection of, and on its top to carry the water-cistern for feeding, the tower. This frame is often employed during the building as a scaffold for hoisting up the stones.

The construction of frame usual on the Tyne is seen in fig. 114 (p. 218). It is bound together at the foot by metal corner-brackets and screw-bolts. The uprights should be at least 9×9 inches thick; the diagonal stays may be weaker. When the frame has been erected, railway-plates are laid upon two opposite crown-trees, and bent up a little at each end. On these runs a bogie, carrying rails at right angles to the first; and on these is put a second bogie, carrying a winch; so that the latter can be run on any given place within the frame most easily and quickly. This travelling crane requires four men to work at the winch.

The bottom stone, which is at least 12 inches thick and very heavy, is best put onto the foundation before the frame is erected; for this the crane is not required, as it can be hoisted by screw-jacks. They are often dished towards the side where the acid is to run away; or a hole is drilled in for the same purpose. The remaining upright stones are provided with two shallow recesses near their upper edge; in these a cramp, attached to the winch-chain, gets a hold. In fig. 119 it can be seen how one arm of the cramp enters into a square hole in one side of the stone, whilst the other side is pressed against by a screw passing through

Fig. 119.



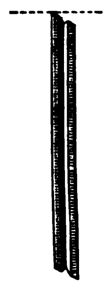
the other arm and by wood wedges. Thus the four stones belonging to each course are hoisted one by one by means of the crane, let down into their places, and provisionally fixed by iron and wooden stays, till the whole course has been completely bound and the joints made good; then the next course is put on, and so forth up to the top; the cover stone is as yet left off, till the packing has been finished.

The courses are built just like those of the stone tanks described on p. 197 *et seqq.*, and may be constructed according to either of the two systems mentioned. Here, however, the horizontal joints between each two courses make the matter a little more complicated. For the first system, that of bevelled corner edges, an india-rubber ring of 1 inch thickness is required for the bottom, and $\frac{9}{16}$-inch or $\frac{5}{8}$-inch india-rubber cords for the upright corner-joints. These are fastened in the four corners of the bottom-ring after adapting this to its groove (p. 198), and are stretched perpendicularly up to the crown-tree; on letting down the stones care is taken that the cords get into their proper grooves. The horizontal joints are made good by strips of flannel soaked for twenty-four hours in a mixture of boiled linseed-oil, red lead (two parts), and finely ground sulphate of barytes (three parts). The latter is added to retard the hardening of the cement. For post condensers, only the bottom course below the grating need have india-rubber cord for the corner-joints; in the rest of the courses all the joints can be made good by soaked flannel strips. The upper and lower edges of all the stones must have a slight slope inwards, say 1 inch, as seen in fig. 120; in this way no acid can run out. All the edges of the stones must be well cleaned by means of a brush, as any small pebbles or rough sand would spoil the joint and do great harm. The necessary binding by means of corner-brackets and screw-bolts is very troublesome, as each single part must be supported until the last nut has been screwed home. Along with the tower a light wooden scaffold must rise up inside, upon which the men may stand.

With the second system the erection is easier, because the stones grasp one another, and especially the binding can be done without any trouble whatever. This advantage is even more important here than for acid-tanks and chlorine-stills. On the other hand, the making good the joints (the horizontal ones especially) is less easy and reliable, because the least carelessness of the man stem-

ming in the "black stuff" does great mischief. For this reason the following very cheap and more reliable way of making the joints is sometimes employed. A V-shaped groove is worked all round the edges of each stone—similarly as in figs. 107 and 108 (p. 200), if the upper and lower edges are made alike, except the slight inward bevel given to the horizontal edges. The side elevation, fig. 120, will make this quite clear. In this way a lozenge-shaped channel is formed wherever two stones touch. As soon as a course is finished, melted sulphur is poured into all the upper openings of the channels; it naturally also runs into the horizontal channels, and affords perfect security against any leakage of acid or gas. The stones, as in joining them by tar-and-fireclay cement, must be perfectly dry; if needful they are dried and gently warmed by means of a fire of shavings. Of course the sulphur would melt if the gas entered the tower much above 112° C.; but that ought never to happen. A tower built in this way should not be exposed to much shaking.

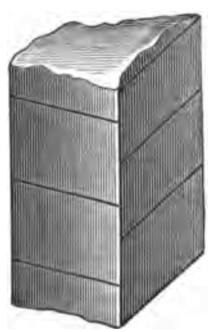
Fig. 120.



Formerly sometimes the horizontal edges were made to lap over (see fig. 121), leaving a space for putting in the tar and fireclay cement; but the system just described is preferable.

Fig. 121.

Fig. 122.



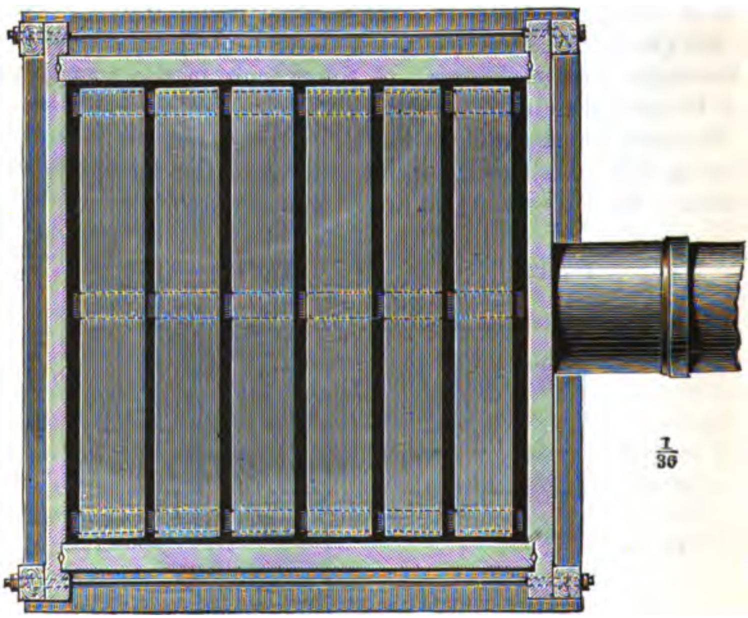
The four stones forming each course are not all made of the same height, but the sides of the first course are made a foot higher than the ends. In the next course the stones are made of equal height, but at unequal levels, as shown in the sketch, fig. 122, and

also in fig. 114. Thus a much better bond is obtained than with joints running all round. This does not affect the sulphur-joints, nor the cutting of the stones, as will easily be perceived. But care has to be taken to place the iron binders always in the best way for making the bond a strong one.

Formerly the courses were made of equal height, but the sides and ends were changed alternately from course to course.

In order to equalize the pressure of the screw-bolts upon the condenser-sides, 6-inch timbers are carried up the whole height of the tower; sometimes these are made stronger, so as to carry the water-cistern. These timbers are not shown in fig. 114, in order not to make it too complicated; they are put along the four cor-

Fig. 123.



ners, so that all the screw-bolts pass through them, as seen on the plan, fig. 123.

The stones near the bottom should be 5 to 7 inches thick, higher

up only 4½ inches, if very good sandstones are available. They are frequently made thicker, especially if the stone is rather soft.

The *iron parts* of the condensers must, of course, be well tarred; and this must be repeated from time to time. In spite of this, bracing-rods &c. are frequently corroded and spoilt by acid oozing out or even by rain-water absorbing some acid when dropping upon them. This is especially dangerous in the bevelled-corner system; for here the corrosion of a single screw-bolt means the destruction of the whole binding all round; and if by chance both the bindings belonging to a course were similarly spoilt, this course, and with it the whole superjacent portion of the tower, would collapse like a house of cards. In the second system, of grooved joints, this danger is nothing like so great; but here also the corrosion of the rods is a serious evil. Sometimes, therefore, all rods, after being well tarred, are further protected by india-rubber pipes, or more cheaply by earthenware pipes put on in building, before the rod has been pulled through the hole of the second stone.

Now and then towers are met with altogether dispensing with

Fig. 124.

iron binders. In each course two opposite stones project above the next lower course, and take hold of it by recesses fitting onto two stones at right angles to themselves, so that the whole is well kept together; fig. 124 will make this clearer. Whatever is saved here in iron, is more than counterbalanced by the extra cost of stones and labour; but there is absolutely no need for repairs, and such a tower should, as it were, last for ever.

In many cases (formerly much more frequently than now) *brick condensers* are employed—in well-managed factories very rarely for strong acid, mostly only for weak acid or as flushing-towers (post condensers). They are mostly cheaper than stone towers—for instance, on the Tyne, where fire-bricks are very cheap; but they very rarely answer all fair expectations, and the author has been told by one of our most experienced alkali-makers that, after trying for many years, he gave up endeavouring to make his brick condensers as tight as stone condensers. Whoever prefers to a saving in prime cost lasting and satisfactory work, and exemption from the trouble of frequent repairs, will build his condensers of stone flags.

For brick towers fire-bricks are mostly employed, because these resist acids better than common bricks; in Lancashire the blue Welsh bricks are commonly used for this purpose. They are set in tar and fireclay, with very thin joints. Sometimes there is an inner wall and an outer jacket, separated by a layer of asphalt; more frequently the walls are solid. Some works employ specially moulded bricks, having a slope of 1 inch in their length of 9 inches. Then the brickwork looks, in vertical section, like fig. 125; inside there are the sloping bricks, outside $4\frac{1}{2}$ inches of plain bricks. At the bottom a whole brick would be taken for the outside. The object of the slope is self-evident; but such towers are said not to have any great advantage over those built of plain bricks. In the latter case the walls on the Tyne are made 18 inches thick up to a height of 10 feet, and 15 inches for the remainder. Three courses of bricks are laid as runners, and the fourth as binders (at right angles to the thickness of the wall). For greater stability, and also for carrying the water-

Fig. 125.

cistern, there are upright 12-inch beams placed in the corners, cut out as in fig. 126, so as to take hold of brickwork. Every 5 feet of height, corner-brackets and binding-rods are provided. A similar kind of binding can also be employed for stone towers in lieu of the frame shown in fig. 114. The bottom of the tower is always formed by a single stone. The condenser is several times painted with tar all over inside and outside.

Fig. 126.

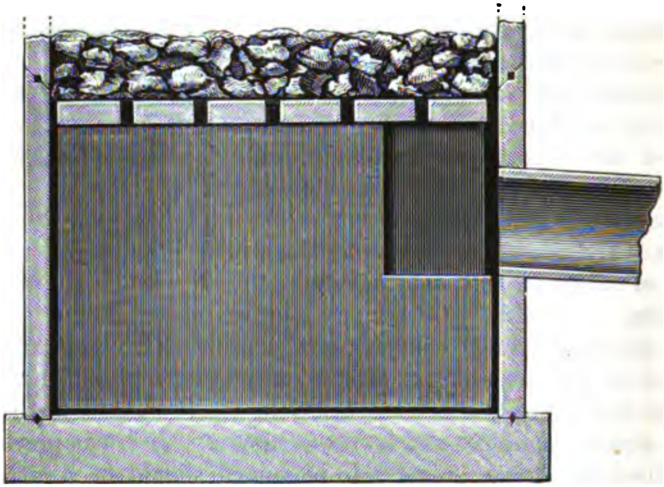
Kopp mentions that condensers might be built of common bricks soaked in hot tar, and immediately after walled quite hot. The weight of the bricks sets them firmly in the thickened tar, which, after cooling, solidifies and serves as mortar. If bricks previously tarred are employed, the faces to be joined should be heated and, immediately before walling, dry sand dusted upon them. This is necessary both as a protection against acid and against their sliding upon one another when the heat gets up. Whether this style has been found suitable in practice, the author has not been able to learn.

In many works the post condensers are not made as high as the strong-acid condensers, but much broader, in an oblong shape, with two or three partitions, alternately open at top and bottom, so that the gas has to travel up and down. This is like three or four adjoining towers; it is not so usual with stone condensers as with brick towers.

The construction of the *grating* or *dome* upon which the packing rests is the same for all kinds of condensers. This grating is either a pigeon-holed arch, made of the best fire-bricks, or it is made according to fig. 127 (and above, fig. 123).

Three stone flags are placed edgeways on the bottom stone; they project above the entrance-pipe for the gas (say 3 feet above the bottom), and are parallel with the gas-pipe; the middle flag is cut out in front, so that the gas is equally spread. The plan, fig. 123, along with the section, fig. 127, shows this clearly. These flags, about 4 inches thick, carry other stones serving as grate-bars, 12 inches broad, 4 to 6 inches thick, and $2\frac{1}{2}$ inches

Fig. 127.



apart. In the case of very high towers, a second, sometimes even a third, grating or dome is built-in higher up, so as to lessen the pressure of the packing upon the lower parts.

If the dome has to be arched, first two dry 9-inch fire-brick walls are carried up 3 feet along the two sides of the tower at right angles to the gas-pipe; upon these a number of 9-inch arches are sprung in a semicircle from one side of the tower to the other, so as to throw the pressure downwards and keep it off the sides. These arches are half a brick wide and distant from each other by the same width (4½ inches); they are connected by special binding-bricks, which pass from one arch to the other, a distance of 12 inches from centre to centre (measured on the top of the arch), and form a continuous course; thus pigeon-holes are formed in the dome. The closers are, in the centre, 9 inches wide, in order to reach from centre to centre of two arches; the end closers must be 12 inches wide; they must be 9 inches high; and their other dimension is 3½ inches at the top and 1½ inch at the bottom. The spandrels are walled up level with the crown of the arches so as to form a plane; and the whole is bound together by a wall of 15 inches height and 4½ thick, running round all the four sides.

The *coke employed for packing* should be of the best and hardest

quality of oven-coke; gas-coke is of no use whatever here, because it is too soft and would soon be disintegrated. Immediately above the grating the largest and longest pieces are placed, and that regularly in parallel courses, the first crossing the grate-bars, the second at right angles with the first, and so on. For each following course smaller pieces are taken, ultimately about 5 to 6 inches by 2 inches, always mixing a few large pieces with them. Since the subsequent action of the condenser essentially depends upon the equal division of water and gas in it, too much care cannot be spent on selecting and arranging the packing; it ought only to be left to a thoroughly trustworthy man. When one third of the condenser has been packed in this regular way, the remaining two thirds may be simply filled by tipping-in pieces of coke, separated from all smalls by a riddle with 2-inch meshes. The coke is filled in up to the lower side of the gas exit-pipe; after some time the packing settles down a few inches.

At first the coke yields up a little iron and organic substance to the acid; afterwards this ceases. After some years the coke-packing must be renewed, notice of which is given by the draught getting bad.

In lieu of coke, special fireclay blocks, perforated with many holes, are sometimes used; also thin earthenware pipes, or pieces moulded in the shape of flower-pots with perforated bottoms and sides. The latter kind of packing is very efficient, if properly carried out, but is rarely employed on account of its expense, except in Schaffner's small condensers (see below).

Now the cover is put on. It consists of one or two stone flags, 3 inches thick, in which a number of holes (say sixty-four for the large condenser and nine for the post condenser) are made, tapering below and serving for the water-lutes, figs. 128 and 130; the joints are made good with red lead. Fig. 129 shows this. The water-lutes consist of two parts—a cup with a $\frac{1}{2}$-inch short open tube in the centre, and a loose cover over this. The whole top is surrounded by a stone edge 8 to 12 inches high, and the wooden oscillating bucket (see fig. 129) fixed upon it. When this has poured its contents over one half of the lutes, they will be filled with water; but all of this that stands above the small central tube runs off directly; the nicks of the small covers allow the water to run in without letting out any gas, as there is still a shallow water-lute left. This periodical running over serves best

Fig. 128.

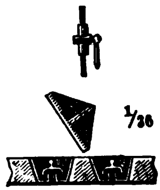


Fig. 130.

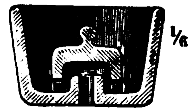
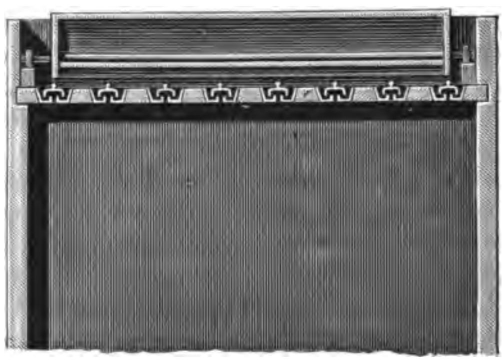


Fig. 129.



for drenching the coke equally. As soon as the other half of the oscillating trough is filled, it turns over again and drenches the other half of the lutes.

This arrangement of oscillating trough and water-lutes is very much to be recommended, much more than simple holes in the top covers, which easily allow gas to get out. A simpler plan is this—putting in the hole a short bit of rope with a knot at the upper end. Sometimes the water is run into the condenser by a single swan-necked pipe, onto a splashing-plate 2 or 3 feet below; but this does not act any thing like so perfectly as the arrangement described above.

When the covers have been hoisted up, the winch is taken to pieces and let down, and the previously fitted planks forming the water-cistern are pulled up by means of a pulley. The planks are of 3-inch pitch-pine, with planed edges; red lead is put upon these before joining them; and all the joints are ultimately well caulked

with red lead and oakum. The bottom-planks, which rest upon the crown-trees of the frame by means of 7 × 3-inch joists, are forced together by wedges, just as in laying the floor of a room. The side-planks are bound to each other and to the bottom-planks by a number of screw-bolts whose heads are visible in fig. 114. Horizontally two sides fit into corresponding grooves of the ends, exactly as in the stone construction, fig. 123 (p. 230); and they are held together by screw-bolts exactly in the same way. In lieu of these cisterns, there are also found ordinary boxes lined with lead; iron cisterns cannot be used in this case.

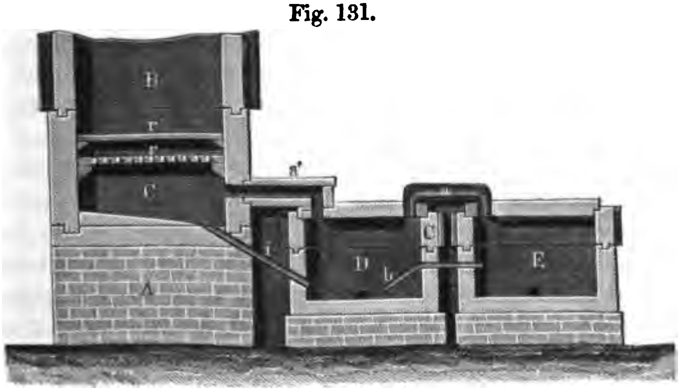
In the bottom of the water-cistern there are two 1-inch water-pipes with cocks *y y*, ending over the centre of the oscillating trough, as sketched in figs. 114 and 128. These pipes project about 6 inches inside the cistern, and are provided with a perforated cap for keeping off mud &c. The cistern is fed from time to time from a 2-inch pipe, usually by a separate small pumping-engine.

All the woodwork, iron, and stone is covered with a double coat of tar or, still better, tar-varnish, to be renewed twice a year.

The condensed strong acid runs off through a 1½-inch earthenware cock just above the bottom of the condenser, and is carried to the stock-cisterns *h h* (fig. 114), which should hold twenty-four hours' make. The weak acid from the post condenser is either run away, or used for some special purpose, or run into the cooling-tanks in order to be got up to strength. Sometimes it is pumped back for use in the strong-acid condensers, as we shall see below.

The connexion between the tower and the tanks may also be made in the way shown in fig. 131 (from Schrader, Dingl. Journ. clxx. p. 183).

Fig. 131.



A is the foundation, B the lower part of the tower; *r r*, the grates; C, space for the gas and the liquid acid, which runs off through *i* into the tank D; *b*, a glass or earthenware overflow from D into E. The acid vapours of course take the opposite direction —from E through *a* into D, and through *a'* into C.

Figures 132 and 133 give an example of coke-towers of a large works; they represent the pan-condensers at the Tyne Chemical Works, Gateshead, from the first Report on the Alkali Act. The section, fig. 132, shows only one condenser; but for the sake of greater stability six, for as many pans, are built together, in two rows of three each, as shown in the elevation, fig. 133. In fig. 132 *a* is the decomposing-pan, working up 10½ cwt. per hour, or about 12 tons 16 cwt. in twenty-four hours; *b* is the string of fireclay pipes; *d d* is the coke-tower itself, 5 × 5 feet wide inside. The height of the base is 5½ feet; that of the stone condenser itself, 100 feet; that of the water-cistern house, 15 feet; and the pipe *k* for the escaping gas projects 3 feet above the roof of this house. The column of coke is divided into three parts by the brick arches *e e*, to prevent the lower strata from being crushed by the weight of the upper ones: for towers of less height these arches are not required. *i* is the exit for the non-condensed gases through the pipe *k*; *l*, a water-cistern; *n*, the oscillating trough; *o o*, a stage on the roof of the cistern-house for getting to the pipe *k*.

In fig. 133, A B C are three of the condensers, D the foundation with the concrete basement E, resting upon the piles F; *a a* the mouths of the gas entrance-pipes, *b b* the stays of the timber frame, *c c* the stairs, G G the cistern-house, *e e* the escape-pipes for the gas.

For smaller works, undoubtedly, the best kind of condensers are those constructed of large *earthenware pipes*, combined with receivers or stone tanks. The pipes are either made of the same stoneware as the best receivers, or of fireclay, and in the latter case boiled in tar. Their joints are made with tar and china-clay; the bottom pipe stands either on a stone cistern or on a solid stone plate in which a groove for that pipe has been cut. This groove is gently heated by a fire of shavings; the pipe is put on, leaving below it a space of about ½ inch, small bits of slate having been put in; the joint is filled with melted asphalt; the cement is pressed in smoothly by means of a hot flat-iron; and, last, for greater safety, it is walled round with a ring of firebricks set in tar. In order

Fig. 132.

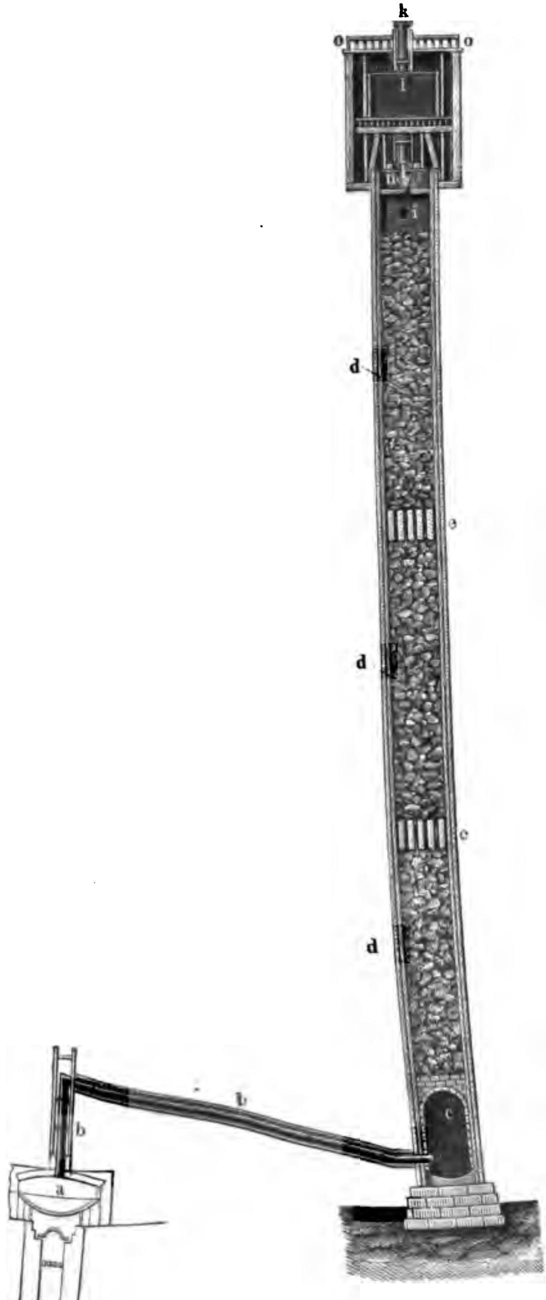
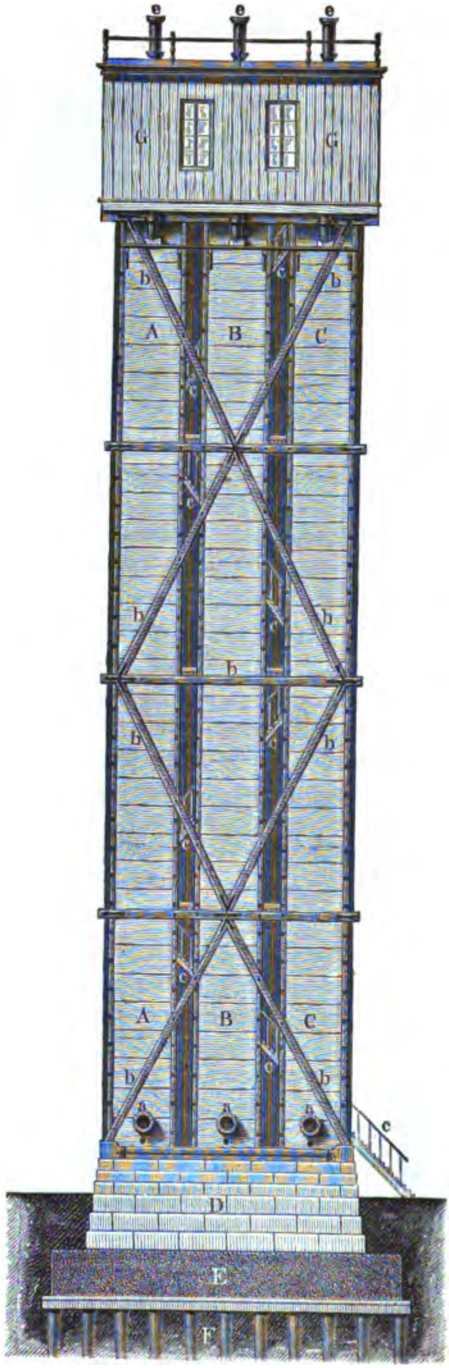


Fig. 133.



not to allow any acid whatever to get to the joint, it is best to dish the bottom stone, and to drill from the lowest point in a downwards slanting direction; into the hole thus formed an earthenware pipe for the liquid acid is introduced. The remaining large earthenware pipes are easily put on; and the joints are all made with tar and china-clay. Each third or fourth pipe should be supported from the timber frame by means of beams placed underneath its socket; thus the bottom pipes need not support the weight of the whole column.

Since a single pipe tower, even of the largest practicable diameter (say 3 feet), is unable to condense the gas from a pan working on the large scale, several such towers should be combined and the gas divided among them by branch pipes. This is done in the simplest way by conveying the gas first into a long stone tank, placed in front of the condensers, from which as many branches depart as there are pipe towers; the same trough serves for collecting the acid and getting up its strength. Or special earthenware vessels for dividing the gas may be provided.

Earthenware condensers are excellently adapted for the gas from pans and from blind roasters; so far the risk has not been run of employing them for open roasters, since the pipes are subject to cracking by too much heat. If this happens, one or two iron hoops are laid round the cracked pipe, consisting of two halves joined by screw-bolts. As these would soon be eaten through by acid oozing out, they are lapped round with tarred spun yarn and the whole thickly coated with tar; moreover they are kept off the leaking place by wooden wedges.

According to the author's own experience such towers need only have two thirds the area of stone condensers—no doubt partly on account of the much better cooling arising from the thinner walls and the greatly increased surface, and partly on account of the better division of the water on the much smaller area of each single pipe.

Sometimes, instead of earthenware coke-towers, apparatus similar to what we have shown, Vol. I. p. 378, fig. 160, for absorbing the nitrous gas in the manufacture of sulphuric acid, are employed. There are in this case within a column of earthenware pipes shelves of the same material fixed, so that the water supplied at the top runs down very slowly, whilst the gaseous current ascends in serpentine windings. But this does not afford any thing like so good a contact

between gas and water as coke-towers, and the advantage claimed for this system, that the draught is less impeded by it than by coke-towers, is rather to be considered a fault (comp. p. 215).

Extremely successful for medium-sized and small works has been the *condensing plan of Mr. Schaffner*, of Aussig—certainly only in consequence of the excellent quality of the receivers and pipes made in that place, whilst an imitation of that plan with bad material would no doubt lead to incessant interruptions for repairs. The manufacturers wishing to introduce this system have therefore, in spite of the cost of transit, got the whole plant from the Aussig Chemical works, which has already supplied 60 complete condensing-apparatus to German, Austrian, Hungarian, and American factories. At Aussig blind roasters are employed, making in twenty-four hours 12 batches of 8 cwt. each. The condensing-apparatus for this is represented in figs. 134 to 137, and consists of the following parts.

The condensing-apparatus for the pan-gas is separate from that for the roaster-gas, especially in order to obtain hydrochloric acid free from sulphuric acid, such, for instance, as sugar-works require. Much more sulphuric acid is present in the roaster-gas than in the pan-gas, as we have seen. If its presence does no harm, such a separation of condensing-plant is unnecessary.

The gas from the pan, being less hot, travels through a flue made of fireclay pipes to the small tower A, fig. 135; the hotter roaster-gas is taken first through a flue made of tarred bricks, then through fireclay pipes into the small tower B. The two towers A and B, built exactly alike, fulfil two purposes, viz.:—first, cooling the gases before they get to the receivers; and, secondly, washing them without subjecting them to any water-pressure. They are provided with a stone grating, below which the gas enters. The whole space above the grating is filled with earthenware dishes of a particular shape, which are four times a day moistened with water by a special contrivance. The sulphuric acid, having more affinity for water, is almost entirely retained here, and nearly pure HCl passes into the proper condensing-apparatus. This consists, for each pan or roaster, of 53 receivers, whose arrangement is shown in the drawings. The first double series of receivers *a* is provided with long connecting pipes (*r r r*, fig. 134) for the better cooling of the gases; in the second double row (*b*, fig. 135) these long pipes are not required. From the receivers the gases pass into an earthenware tower, entering underneath a grating inside the same. The tower is two-

thirds filled with earthenware dishes as above; the uppermost third contains coke. On the timber frame of this tower a water-cistern (R, fig. 137) is placed, from which the water issues by means of a turbine distributor, moved by the falling water itself and spreading it all over the tower. From each tower a pipe carries the residual gases downwards; and both systems (for the pan and the roaster) ultimately unite in the large receiver P, fig. 135; from this a pipe descends into a flue leading to the chimney.

In order to observe and examine the exit-gas continually, each system is provided with a "sight," closed by glass panes, visible in fig. 136 at *l l*. In these at the same time the draught can be regu-

Fig. 138.

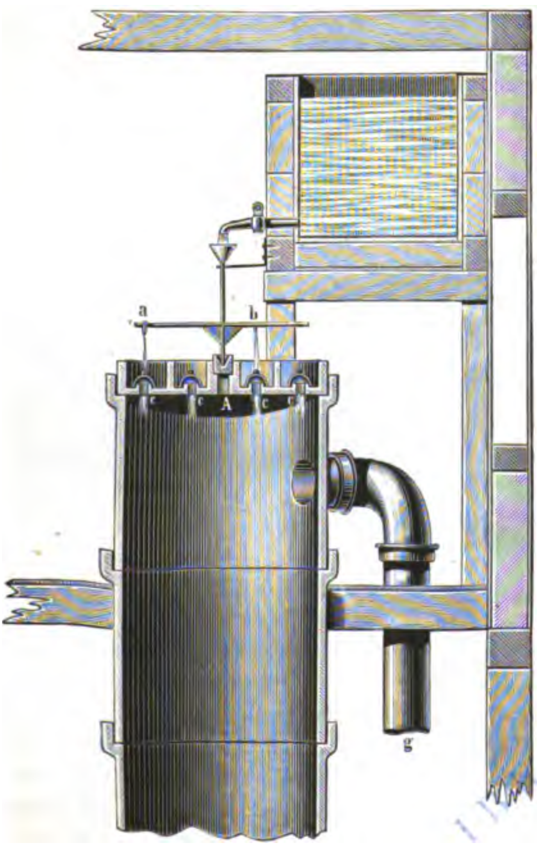


Fig. 139.

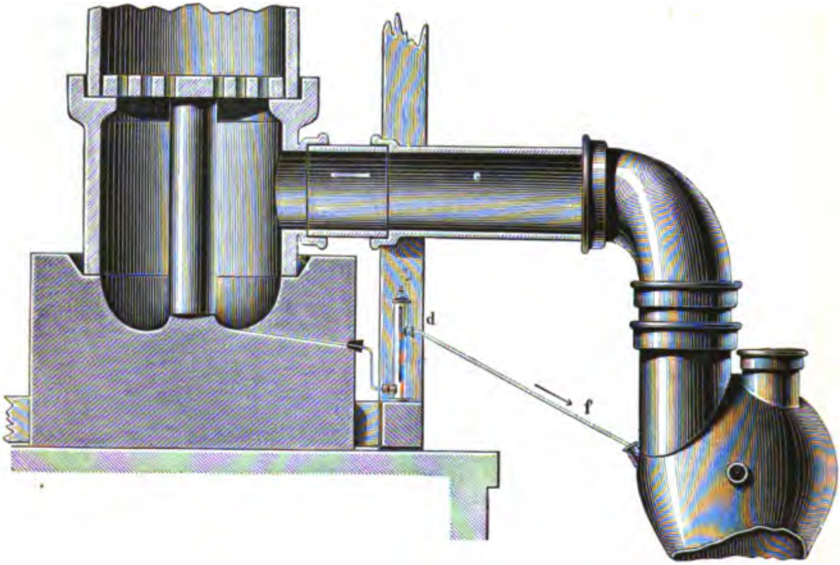
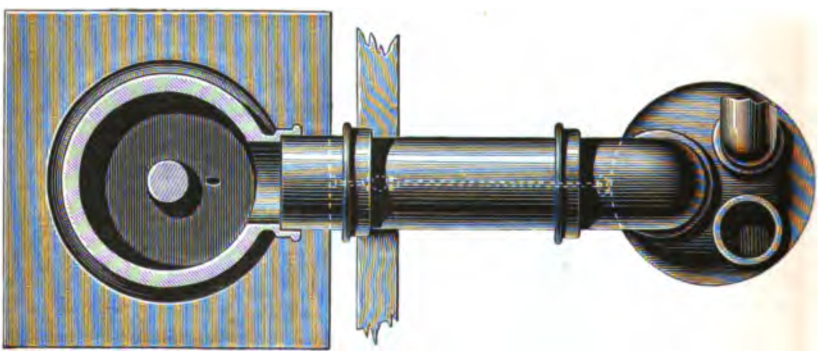


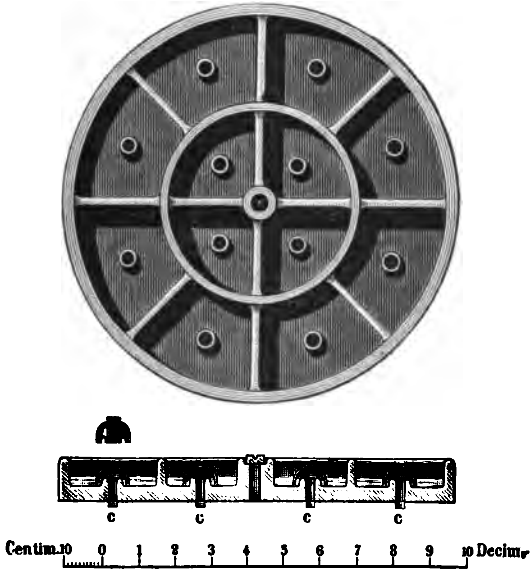
Fig. 140.



lated by putting more or fewer plugs into the grating with round holes, lying in the sight (compare Vol. I. p. 330).

The acid issues from the tower 12° Tw. strong, runs through all the receivers, and arrives in the first receiver 35½° Tw. strong. The acid condensing in the small towers A B is run off separately by stoneware cocks. In order to check the process, glass cylinders

Fig. 141.



are interposed in several places, through which the acid runs, and in which hydrometers show the progress in the percentage of HCl.

Figs. 138 to 141 give some details of the construction. Fig. 138 shows one of the towers in sectional elevation, through E F in fig. 135; fig. 139, the same, cut across the gas entrance-pipe; figs. 140 and 141, the cover of the tower with its compartments. The distributing wheel empties its contents of water through *a* into the outer, through *b* into the inner compartments of the cover; *c* are glass tubes cemented in; *d* is a hydrometer for the acid running off; *e*, the gas entrance-pipes; *f*, the pipe for running off the acid; *g*, the gas exit-pipe.

Figs. 142 to 147 give all the details of the small preliminary tower. *w* is the injecting pipe, coming from the water-main, H the cock for running off the acid, E the entrance-pipe of the gas.

According to Dr. Angus Smith, whose experience in this matter no doubt exceeds that of any one else, a condenser of 50 feet height and 5 feet square suffices for the gas given off by decomposing 5 tons of salt in twenty-four hours, if the supply of water is properly regulated. This refers to blind roasters. Dr. Smith even prefers another condenser of equal size for the roaster itself; but this is

Fig. 142.

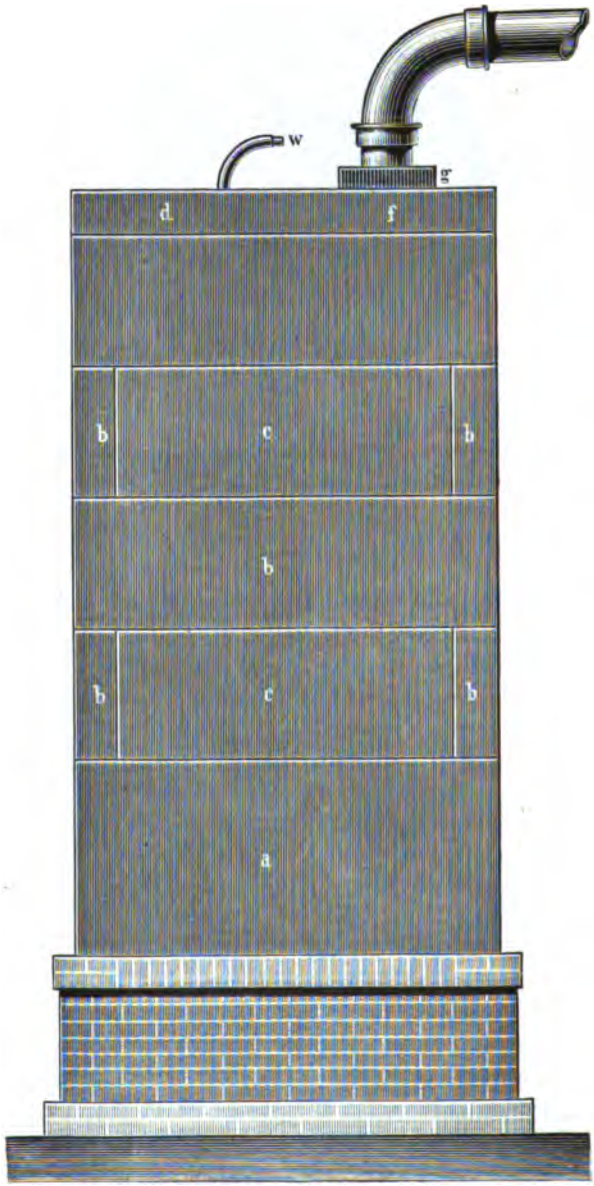


Fig. 143.

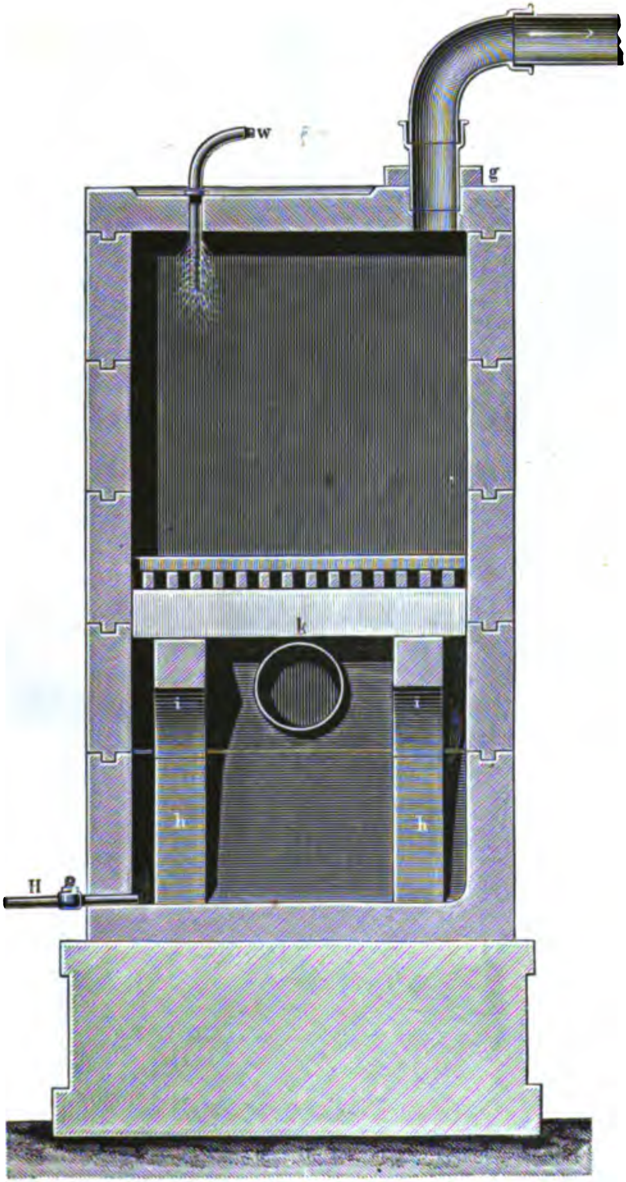


Fig. 144.

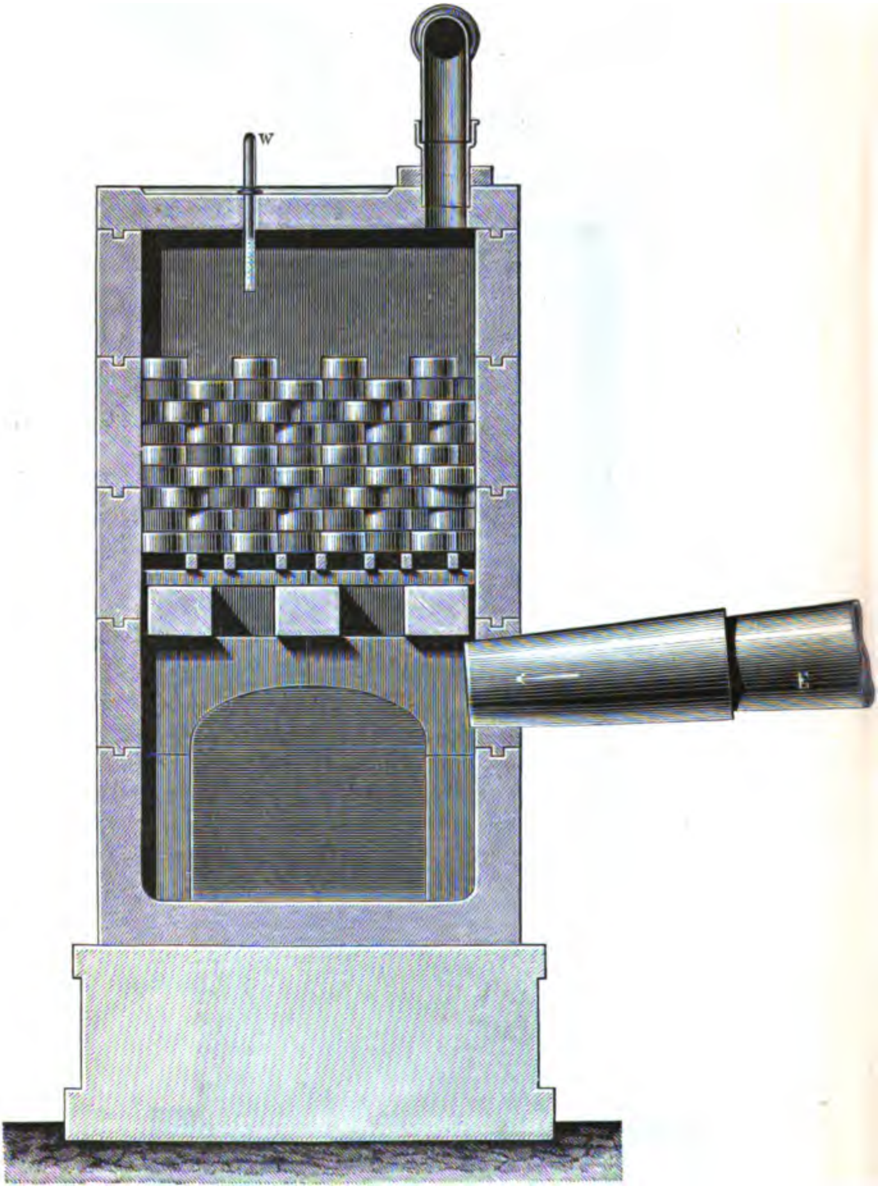


Fig. 145.

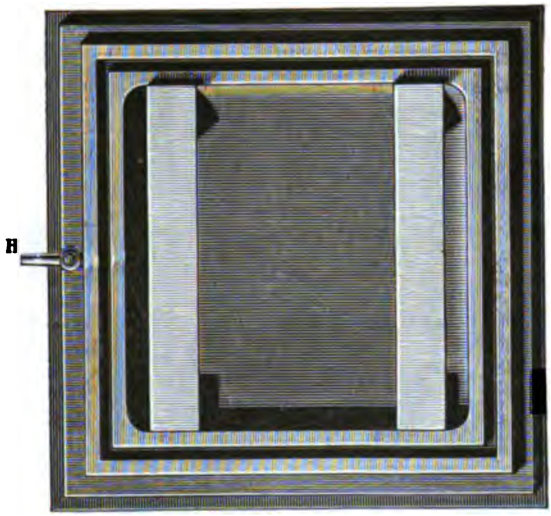


Fig. 146.

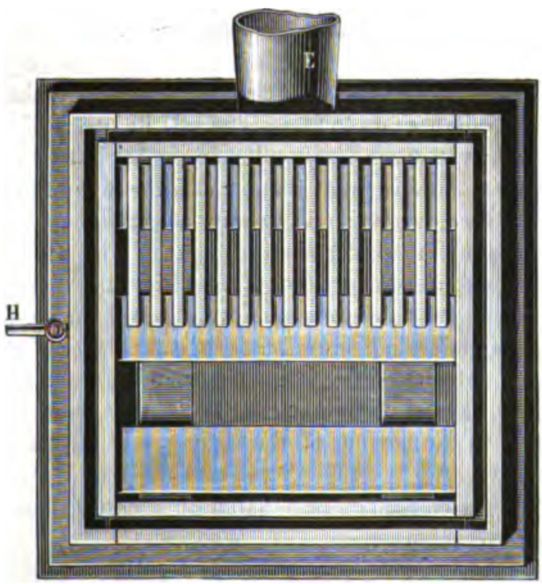
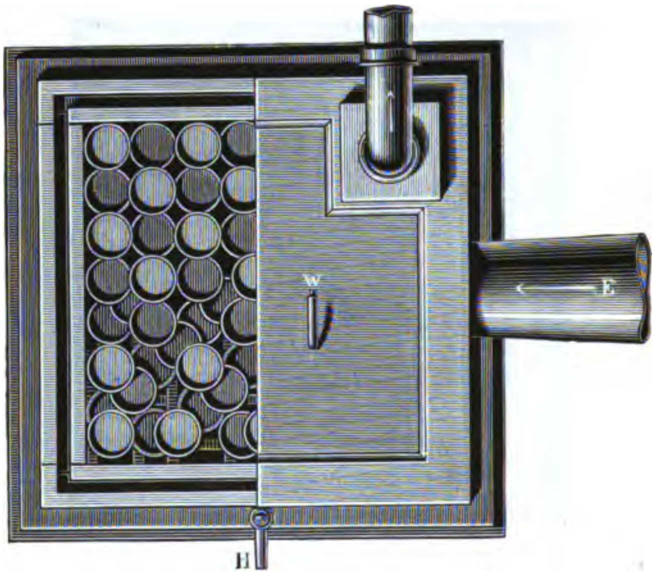


Fig. 147.



doubtless not absolutely necessary. It may be safely asserted that for *two* pans, if alternately worked with regularity, a condenser of 6 by 6 feet section and 50 feet high is quite sufficient, especially if the gas previously passes through two or three acid-tanks; even if the two pans decompose up to 20 tons of salt in twenty-four hours. In case of need, even much less condensing-space has been found to suffice; but then there is great danger of an escape of acid vapour at the slightest carelessness; and in any case the quantity of strong acid obtained is much smaller than it ought to be. It is, no doubt, preferable to make the tower 60 or 65 feet high, because then more and stronger acid is got; some works even have them 100 feet high; but this is inconvenient and unnecessary, at any rate if acid-tanks are employed. At one works possessing such high condensers, two of 50 feet each have recently been built, the gas passing from the top of the first to the bottom of the second, and out of the top of this into the air. All this refers to stone condensers; earthenware pipe condensers only require two thirds of the sectional area, but the same height.

Chandelon gives the following details for Belgian factories, relating to the year 1871 and to pans and roasters together :—

	Cubic capacity of the *cooling-apparatus* for each 100 kilog. salt decomposed in 24 hours. cubic metre.	Cubic capacity of the condensers themselves. cubic metres.
I.	0·378 to 1·480	2·400 to 3·400
II.	0·438 „ 1·001	1·373
III.	3·380 to 4·720	
IV.	0·826 „ 1·000	1·770 „ 2·680

A very large number of detailed statements on the dimensions of condensers in English alkali-works are found in the first three Reports, and *passim* in all the succeeding reports by the Inspector on the Alkali Act.

Condensers for the gas from *open roasters*, if strong acid is to be got from them, should be as high as, but wider than, pan-condensers; if only weak acid is aimed at, they are usually made much lower (20 to 30 feet high), but of so much the larger area. Frequently they are made of bricks, but better of stones—the gas being previously cooled, lest the stones should crack. Where furnace-gas has to be condensed by an excess of water, Dr. Smith states that a condensing-space of 4 cubic feet for each cwt. of salt decomposed per diem is sufficient; and this is found true in practice.

A special instance of condensers for open roasters, at the works of Messrs. J. Hutchinson and Co., Widnes, is represented in figs. 148 and 149, showing also how the foundations are made on bad ground.

Condensers made of earthenware pipes are not applicable to open roasters; otherwise they are probably not only the most efficient, but also the cheapest of all; but for very large factories (in England at any rate) stone towers will be preferred for the sake of simplicity, which consideration will probably outweigh that of a larger prime cost. For the same reason all *mechanical means* for promoting condensation will, in all probability, remain unsuccessful. They all cost too much, and give occasion for incessant repairs. Several such have been proposed—for instance, forcing by a fan-blast through finely perforated plates immersed in water (Atkinson's patent, July 14, 1855).

We have already alluded to Clapham's process, which consists in utilizing the extremely dilute acid of post condensers for supplying the proper condensers; thus not merely is the weak acid recovered, but a corresponding quantity of water is saved, and the contamination of watercourses by the weak acid is got rid of.

Fig. 148.

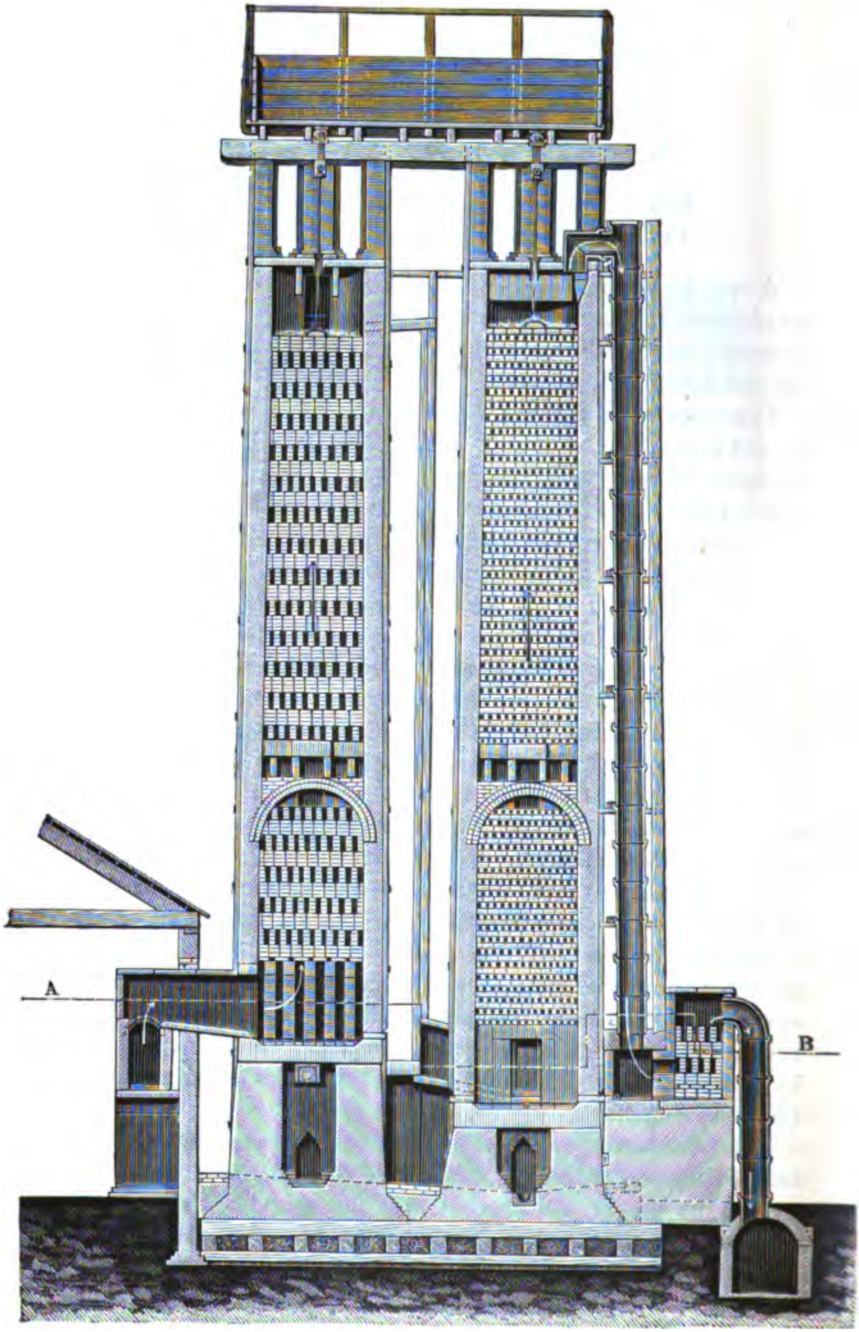
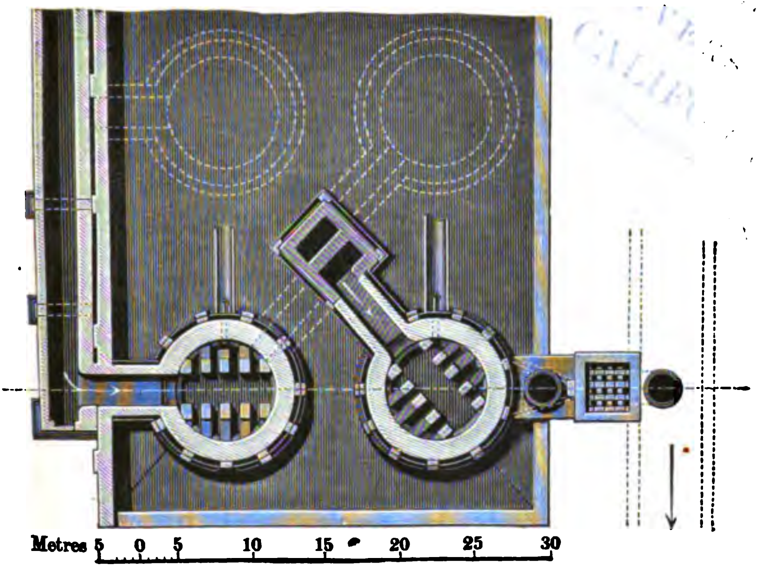


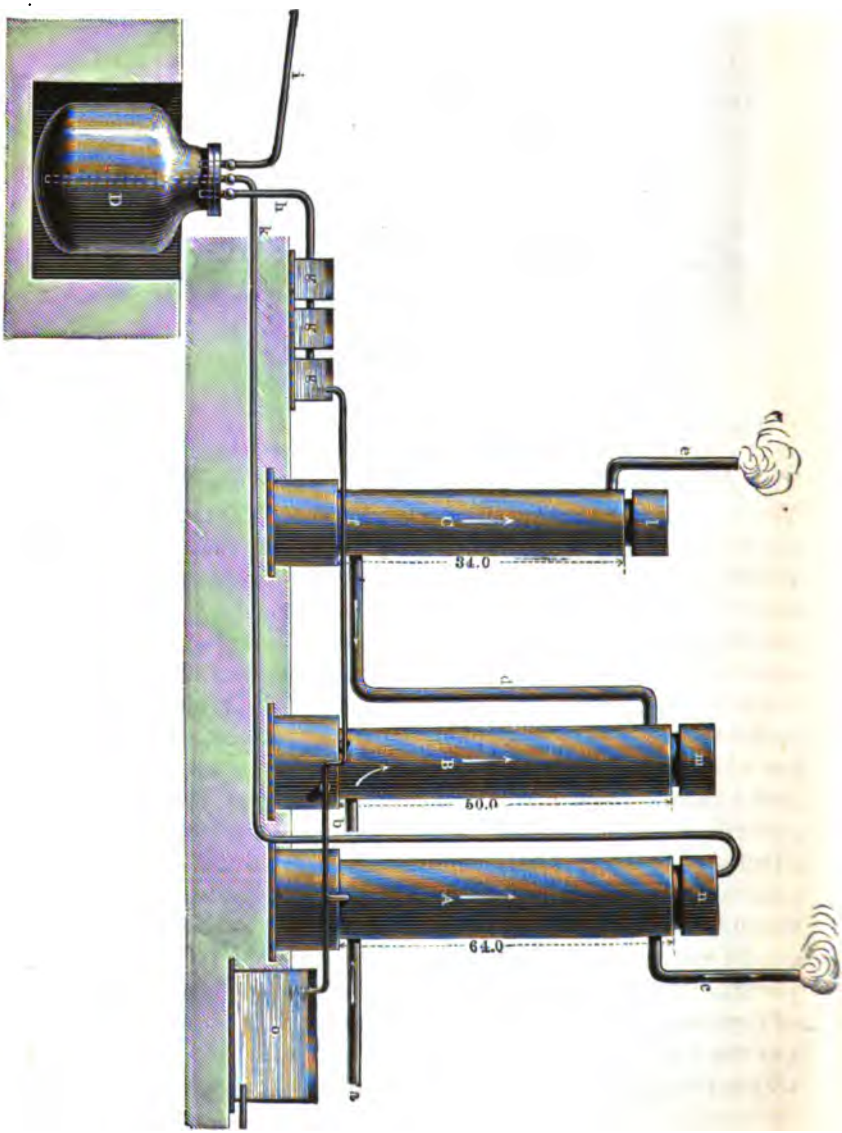
Fig. 149.



This process was in operation for some years at the Walker Alkali Works, now laid in for three pans, producing 150 tons of sulphate per week. The pan-gas passed through two stone condensers, in which its acid was completely absorbed; these were fed by the weak acid from the two roaster-condensers 3 and 4. The furnace-gas first went into the two roaster-condensers 1 and 2, fed with weak acid from 3 and 4, and then into the latter. The acid from the two pan-towers and the roaster-condensers 1 and 3 was collected as strong acid in three large stone cisterns, and employed for chlorine-making. The weak acid from the roaster-towers 3 and 4 runs through a common earthenware pipe into four stone cisterns, in which it is somewhat cooled. Each cistern can be filled or emptied by itself by means of cocks. Their common exit-pipe is divided into two branches, to get more surface, and carried through a trough 40 feet long, in which the acid is sufficiently cooled not to injure the following apparatus, all lined with gutta percha. The cooled acid is pumped upon the condensers by means of compressed air, in precisely the same manner as sulphuric acid; but the "acid-eggs" here must be lined with gutta percha, for which reason the acid must be carefully cooled. (Vulcanized

india rubber would have given less trouble.) Fig. 150 gives a sketch of this arrangement. A is the pan-condenser, fed with weak acid from C; this condenser, serving for roaster-gas, is fed with

Fig. 150.



water. B is the other roaster-condenser, fed with water (or if there is sufficient weak acid, with the latter). *a* conveys the pan-gas, *b* the roaster-gas; *c* carries the residual gas of A into the air, *d* that from B to C, *e* that from C into the air, *f* the weak acid to the cooling-cisterns *g g g*. D is the cylinder lined with gutta percha for forcing up the weak acid, with the inlet-pipe *h*, the air-pressure pipe *i*, and the delivery-pipe *k*; *l* is a water-cistern, *n* a weak-acid cistern; *m* serves for either, *o* for the weak acid from A.

This system was not connected with any chimney, a 12-inch pipe on the top of the roaster-condensers sufficing for carrying away all the gas. The process combines perfect condensation with the production of nothing but strong acid; but the plant is costly and easily damaged. Wherever the weak condensers can be so placed, owing to differences of level, that the weak acid can run into strong condensers by natural fall, all the objections against this plan vanish; and any more easily managed pumps (comp. below) would greatly contribute to facilitate the process. It practically comes to the same as making the condensers of double height, which entails least labour in working, but a very costly and not always very stable construction.

Acid-pumps.

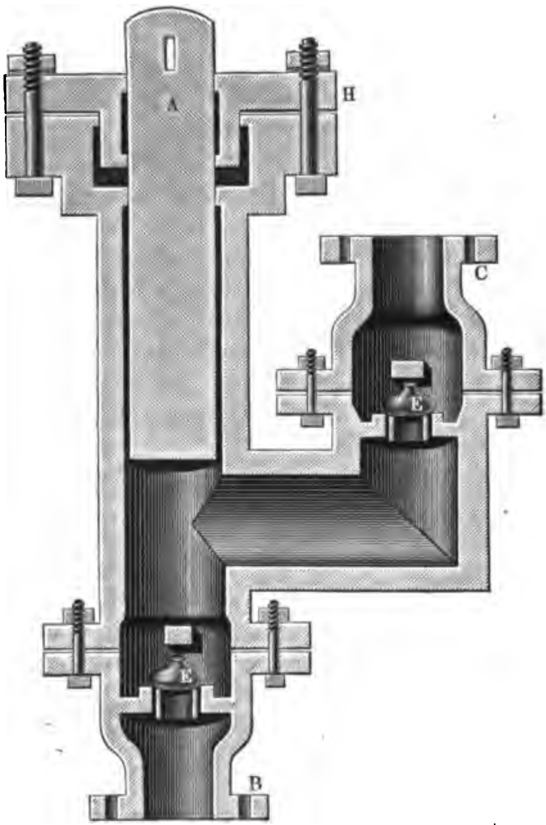
Already in laying out a works care must be taken, if at all possible, to provide sufficient *fall for the hydrochloric acid*; it should find its way from the towers to the tanks or receivers, from these to the store-vessels, and ultimately to the chlorine-stills by natural fall. This is all the more easily attained as the elevation of the gas from the decomposition-apparatus costs nothing at all, and that of the water for the condensers very little. Even where there are no natural differences of level in the works available for this purpose, but artificial foundations, stages, &c. must be provided, the prime cost of these should nearly always be disregarded in comparison with the everlasting expense and trouble of pumping up the hydrochloric acid, which have prevented Clapham's process from being generally adopted anywhere.

Still a number of acid-pumps have been constructed, which are sometimes resorted to, especially in cases where, in consequence of alterations made subsequent to the erection of the works, no natural fall could be arranged for the hydrochloric acid. Apart from the acid-eggs lined with gutta percha, which are both expensive and easily damaged, we should mention the pump made by

Perreaux, of London, with a glass barrel and india-rubber valves. It can only be employed for dilute cold acid, as hot strong acid quickly dissolves the lead mountings.

The pumps made by Doulton and Watts (fig. 151), entirely of

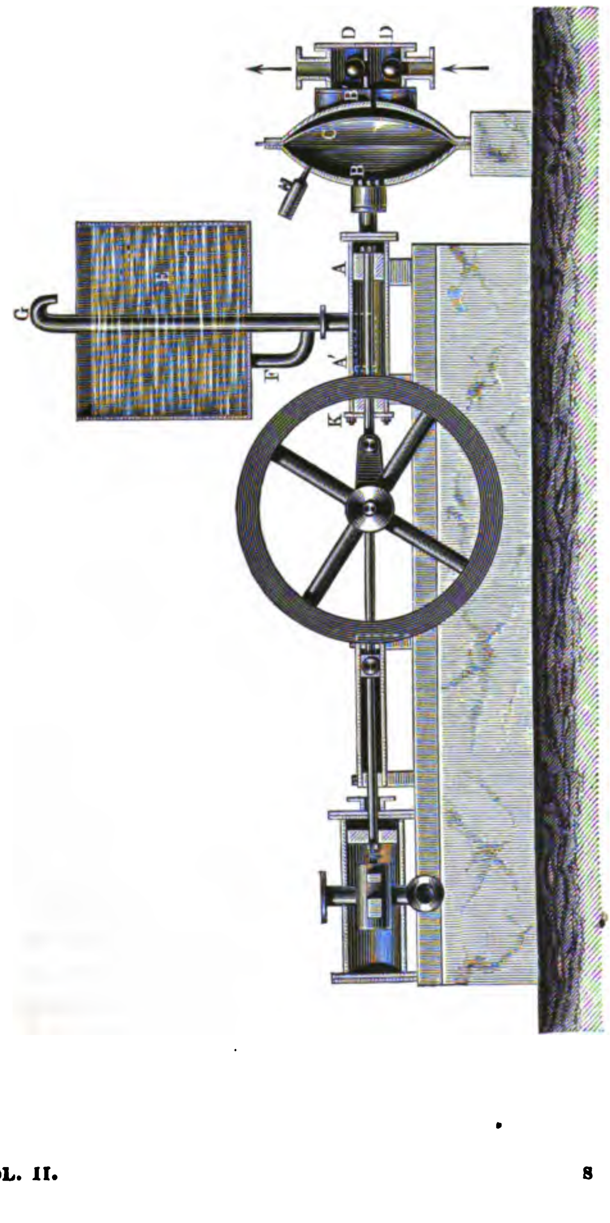
Fig. 151.



earthenware, are not destroyed by the acids; but they are easily broken and are not tight; so that, after trial, they have been discontinued in some places.

The system of Mr. Geo. S. Hazlehurst, of Runcorn, appears to have been more successful. Of the different constructions mentioned in his patents of 1874 and 1876 we only show the most recent, fig. 152. A A′ is an ordinary pump-barrel; B B′ are two cast-iron saucers; C, an india-rubber diaphragm, separating the

Fig. 152.



two saucers so that neither liquid nor air can pass from one side of the diaphragm to the other. D D are india-rubber ball-valves, the lower one for the acid suction-pipe, the upper one for the delivery-pipe. E is a water-cistern, communicating by F with the side A′ of the pump-barrel. When the pump is set in motion, the diaphragm C waves to and fro, drawing and forcing the acid through the valves D D. At each *back* stroke the water in A′ shoots up the pipe G and is delivered into the top of E; at each *forward* stroke the water fills A′ from the bottom of the tub through F. Thus the water is constantly changed without any valves whatsoever, avoiding the drawback caused by the inevitable entanglement of air passing through the gland K. The acid feed-cistern may be placed either below or above the pump; in the latter case an air-vessel is required on the suction-pipe. All parts requiring it are lined with india-rubber (or might be made of earthenware). This pump is specially intended for pumping back the weak acid to the strong acid, thus sparing both water and a source of pollution of streams. It is well spoken of by practical men, and is both much simpler and cheaper than Clapham's plan.

An excellent pump is that constructed by Schlotter, which has now been at work for some years at Aussig, and serves for pumping the *strongest* acid from the store-vessels to the stills, about 20 feet high. The acid runs into a large earthenware jar, into which dip three perpendicular 1-inch glass tubes, of a length corresponding to the pumping-height, of course made of several lengths joined together. These are constantly jerked up together about 6 inches by a small engine, and let down immediately afterwards. By the jerking the acid is thrown up in the pipes, and cannot run back again, because it is retained by a simple india-rubber clack valve contained in a short earthenware pipe at the top; above this the glass tube rises an inch or two, and then bends down (in the shape of a horse-shoe) and dips with its other end into an earthenware jar, into which the acid is discharged, and from which it is run away as required. This pump has, as will be seen, neither a barrel nor a ram; and the valves are reduced to the simplest possible form; it has been proved perfectly efficient by several years' work. The figures 153 to 155 will show its construction more clearly.

We will also mention in this place the peculiar kind of *con-*

nexion of acid-pipes employed with very great success at Aussig. In lieu of cementing and stemming, the joints are made by an india-rubber ring put round the spigot end of one earthenware pipe, which is put into the faucit end of the next pipe with a certain degree of friction. This joint is not only perfectly tight, but gives to the whole length a certain degree of flexibility. The pipes themselves may be made of earthenware, or even of glass.

CHAPTER VIII.

CONTROL OF CONDENSATION; PURIFICATION, APPLICATIONS, AND CONVEYANCE OF HYDROCHLORIC ACID.

THE labour connected with the condensing-apparatus is of a very simple character, and confined to the observation of two matters, viz. first, the completest possible condensation of all the HCl contained in the gas; secondly, the production of the largest possible quantity of *strong* acid. Sometimes, as we have seen above, the second of these conditions is not required. If the cooling- and condensing-space be insufficient, or the apparatus constructed in an unsuitable manner, the two conditions just mentioned are hostile to each other: in such a case, if all the HCl is to be condensed, far too much water must be employed, and therefore no strong acid can be got. With proper condensing-appliances, such as have been described in the preceding Chapter, the all but complete condensation of the *pan-gas* at least (say within ½ or 1 per cent.) can be most justly demanded, and that all to *strong* acid. The *roaster-gas*, from both close and open roasters, can also be completely condensed, but usually, with blind roasters (and with open ones always) only by the aid of a post condenser. A large quantity of acid is obtained in a very *weak* state, and can only find very limited application. It is especially used where the strong acid would have to be diluted—for instance, in making sodium bicarbonate, and in recovering sulphur from the tank-waste; but in this case usually some strong acid must be added. It is further employed in extracting the copper from burnt pyrites (for which mostly enough acid is obtained in the process itself), for purifying coke, iron-ores, and clay from some injurious matters; but it is only rarely possible to employ weak acid for such purposes,

since its small value could not bear the comparatively enormous expense of package and transit. On the other hand, the minerals, ores, &c. will rather be taken to the works and there treated with the weak acid. Thus, for instance, at Stolberg the weak acid is used up at the works themselves for purifying zinc-ores. A similar step would, no doubt, be taken if the procedure proposed by J. Maxwell Lyte (patented February 15, 1877) should turn out successful. He proposes that the mixed ores of galena and blende, which, even when containing some silver, often do not pay for smelting, be digested with "moderately concentrated" hydrochloric acid and steam till the zinc and iron are dissolved along with some lead chloride, which crystallizes out on cooling. This, together with the principal portion of the lead remaining in the residue, is smelted for lead; the solution of $ZnCl_2$ is precipitated with lime at a boiling heat; the $Zn(OH)_2$ is pressed into bricks and also smelted as usual [which is a very difficult operation with oxide obtained in this way].

In any case alkali-makers regularly try to confine the production of weak acid to a minimum, which is only possible by a rational system of cooling and condensing; and to that endeavour the feeding of the strong condensers with weak acid (comp. last Chapter) must be referred.

The control of the condensation will have to take account of both the conditions laid down for it. The acid running out of the condensers, tanks, or receivers ought to be strong enough—that is, for sale acid in winter, 34° to 36°, in summer 30° to 32° Tw.; for own use, acid of 23° to 28° is frequently sufficient, but mostly the higher strength is preferable. Usually samples are taken several times a day and tested by the hydrometer; but it is best to run all the acid coming from the condensing-apparatus through a glass cylinder in which a hydrometer floats, so that a single glance shows the strength of the acid without the time and trouble of sampling.

It should not be overlooked that hydrochloric acid cannot easily be obtained of the highest strength unless sulphuric acid of, say, 140° or 144° Tw. is employed for decomposing; otherwise too much steam has to be condensed.

Nor should it be forgotten that the hydrometer at a high temperature indicates much less strength than at a lower one; according to the Table given on p. 177, an acid which at 19°·5 C. shows

20° Tw., at 100° C. would only show 12° Tw. The acid before testing must therefore be cooled down to ordinary temperatures.

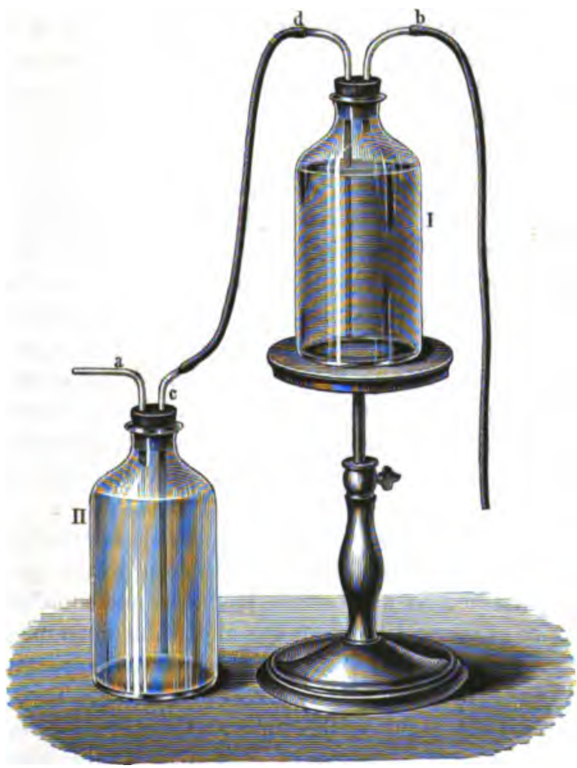
Of the greatest importance is testing for any uncondensed acid gas escaping. What ought to be the maximum of this has been mentioned on p. 189. In somewhat damp air a practised eye can draw a conclusion on the escape of gas, from the appearance of the vapours issuing from the apparatus. It is true that from the open exit-pipes of pan condensers, even with perfect condensation, small puffs of cloud always escape; but this is only steam, and is distinguished from acid vapour by at once dissolving in the air and dispersing. Acid vapours, on the other hand, form thick white mists which, in damp weather, drag along for great distances and keep together for a long time. Frequently these mists are only formed when the gas comes into contact with the outer air.

Of course the appearance of the gases is insufficient for controlling the condensation; chemical tests must be added to this. It would be most satisfactory if, on the one hand, the absolute volume of the escape gases were accurately known, and if, on the other hand, measured portions of the gas were continuously conducted through some absorbent. The first, viz. the getting at the absolute volume of the gases, is very difficult, even with the anemometer of Fletcher or that of Swan (which have been described in vol. i. pp. 331 and 340). Even the continuous taking and measuring of samples is not quite easy; it is best done, according to Mactear, by a small gas-meter, which, in order to prevent corrosion of its parts, is placed *behind* the absorbing apparatus. Any ordinary aspirator of sufficiently large size will fulfil the same purpose in a cheaper way, and is less liable to get out of order. Kuhlmann fils (Année Industrielle, 1878, p. 67) proposes to measure the speed of the gases by evolving coloured vapours at the foot of the chimney, and observing the time which they take in getting to the top.

Usually, however, only a certain volume of gas is aspirated, first from the entrance-pipe and then from the exit-pipe of the gases, and the proportion of HCl in both is estimated. For aspirating, the Alkali Inspectors employ small finger-pumps made of india-rubber balls, which on compression give up nearly constant quantities of air. Standing aspirators are preferable; a very simple and cheap apparatus of this kind is represented in fig. 156. It consists of two glass bottles, I. and II., say "Winchester

quarts," provided with a twice-perforated cork or india-rubber stopper, through which passes one elbow-tube ending just below it, and another reaching down to its bottom. We will call the former *a* and *b*, the latter *c* and *d*. The tubes *c* and *d* are connected by an elastic tube; another elastic tube connects either *a* or *b* with the apparatus through which the gas is to be aspirated—say, with

Fig. 156.



a small Woulfe's bottle containing water and connected also with the outlet of the condenser. One of the bottles, say I., is placed so that its bottom is raised above the neck of II. If now *b* is connected with the absorbing apparatus, and the air is sucked from *a* for a moment, the siphon formed by *c d* and the elastic tube begins to run, whilst gas is aspirated from *b*. When the contents

of I. are run out, the elastic tube is detached from *b*, the position of the bottles is changed, so that II. now stands higher, and the elastic tube is put upon *a*; the connexion between *c* and *d* is not touched. If the attendant sucks for a moment at *b*, the apparatus starts working again; usually sufficient water remains in the tube *b* in the shape of beads to make the siphon start of its own accord. The quantity of water running out of the bottles, independent of that always remaining at their bottom, is determined once for all; or a more exact scale can be put upon the bottles themselves.

For absorbing the acid gases either distilled water, or weak soda solution, or a measured quantity of standard silver solution is employed. In the latter case Gay-Lussac's shaking process must be applied; in the former case Mohr's process, with potassium chromate as an indicator, can be used, if modified for this purpose. Some SO_2 is always present, not only in the fire-gases, but also in the condenser-gas not mixed with fire-gas, probably from the action of sulphuric acid vapour upon the coke. Even small quantities of SO_2 make Mohr's process impossible for direct use. But it can be employed if to the liquid a diluted solution of permanganate is carefully added till the pink colour just appears. All the SO_2 is now oxidized to SO_4H_2; the liquid is neutralized with soda, a very slight excess of which does no harm, no more than the extremely small excess of permanganate; potassium chromate is added, and the liquid titrated with standard nitrate of silver.

To ensure complete absorption of the smallest quantity of HCl in the large volume of gas, a simple bubbling of the gas through the liquid contained in a Woulfe's bottle is not sufficient; but a larger surface of contact between gas and water must be obtained. This is very well done, for instance, by the small apparatus shown in fig. 157, and first introduced by Mr. Glendinning. The gas enters at *a* as usual; it leaves the bottles through the wider tube *b*, which is connected with the aspirator at *c*: *b* is blown into a bulb at the bottom; and a number of small holes are made in that bulb. The whole tube is filled with broken glass. It is put down just to the level of the liquid; the current of gas carries some liquid through the fine holes into *b*, where the gas and water are mixed into froth by the broken glass and come into intimate contact. The tube *b* should be pretty long, as the liquid is sucked up into it to a considerable height. For the perforated glass ball an open glass

tube, closed by a cork with fine longitudinal nicks, may be substituted.

In order to take the samples, there must be 1-inch holes drilled in suitable places of the gas-pipes, of course usually closed in some way. For testing, a cork is put in which contains a glass tube reaching to the middle of the gas-flue, and so placed that no drops

Fig. 157.

of liquid can fall into it; this tube is connected outside with the absorbing-apparatus, and the latter with the aspirator.

Dr. Smith (in the Elventh Report on the Alkali Act, p. 40) gives a special instance of the condensing process as observed at a works at St. Helen's, decomposing daily 6 tons 12 cwt. of common salt, which ought to produce 76·16 cwt. of dry HCl or 253·88 cwt. of 30-per-cent. acid of 31° Tw. It appears that there is a blind roaster, and that both pan- and roaster-gas pass into the same condenser. First they pass through a small cistern close to the furnace, in which in 24 hours about one third of a cubic foot of

27-per-cent. acid is condensed; it is very impure, and its temperature is 46° C. In a second, more distant cistern in the same period 48·1 cubic feet of 31-per-cent. acid at 32° C. collect; the condenser furnishes in 24 hours 400 cubic feet of 29-per-cent. acid at 54°·5 C. The percentage of HCl and steam in the acid gases was twice examined, and found as follows (I. evidently during the most, II. during the least energetic evolution of gas) :—

I.

	grams H_2O in 1 cub. metre of gas.	grams HCl in 1 cub. metre of gas.
3 feet from the pan	1109·27	1511·99
Near the roaster	44·35	304·53
On entering the condenser .	51·06	293·38

II.

	grams H_2O in 1 cub. metre of gas.	grams HCl in 1 cub. metre of gas.
3 feet from the pan...........	146·0	129·66
Near the roaster	1·46	65·45
On entering the condenser...	16·23	37·85

The temperature of the pan-gas was 180°, that of the roaster-gas 315° C., on entering the tower 60° C. In spite of this, as we see, at the latter place only one eighth of the HCl is condensed; and the tower has to perform the other seven eighths of the condensation.

Very important is the regulation of the draught, if the condenser does not communicate directly with the atmosphere, but with the chimney. In any case there must be in the connecting flue a damper of glass, slate, stoneware, or lead, which is opened exactly so far that the gas can just pass through and does not blow out of the working-doors of the furnaces. If more draught is given, uncondensed HCl gas inevitably gets into the chimney, even with an excess of water. In some works the damper is put under lock and key, because the furnace-men are apt to open it more widely in order to get more draught. If, on the contrary, the draught is not sufficient, which mostly happens when the coke

packing has settled down too much, the evil can be cured either by a steam jet in the exit-pipe or by a water jet acting in the manner of a "Bunsen pump" as an aspirator.

The *results* of working the condensers have had to be mentioned several times before, particularly the unsatisfactory ones of former condensers. Few works possess any contrivances for exactly measuring the acid produced; only where all of it is sold can a complete check be obtained. So much is certain, that with really good condensing-apparatus by far the largest portion of the HCl given off can be recovered. Theoretically 100 parts of NaCl would yield $\frac{36{\cdot}46 \times 100}{58{\cdot}46} = 62{\cdot}36$ dry HCl, or, expressed in acid of 34° Tw. (=32·3 per cent. HCl. at 0° C.), 193 parts of such by weight, or nearly 165 litres for 100 kilog. pure NaCl, =368 gallons per ton. Common salt of 93 per cent. would theoretically yield 179·5 kilog. or 153·3 litres (at 0° C.) of the above acid, =343 gallons.

On calculating the acid to be obtained per ton, not merely the percentage of the common salt employed, but also the NaCl left in the sulphate must, of course, be taken into account. This, on the average of most works, amounts to 1·5 per cent., leaving as *possible* yield of hydrochloric acid still 176·8 per cent. by weight or 151 litres per 100 kilog., =337 gallons per ton.

Of the many statements of the *actual* yield of muriatic acid, only a few shall be repeated here. H. Allhusen (Richardson and Watts, vol. v. p. 285) states the result of six accurate trials on the large scale, as follows:—

68·60	per cent. of the theoretical yield from the pan-gas.
29·40	" " " roaster-gas.
2·00	per cent. loss.

Clapham (ib. 260) states as the result of six months' accurate observations:—

100 parts of common salt yielded...........	55·80	HCl.
Left in the sulphate	1·52	"
Loss..	0·58	"
Possible yield	57·90	"

At Messrs. Garrett's, of Wigan, there were condensed:—

In the stone cisterns	66·04	per cent.
„ receivers following them	33·396	„
„ coke-tower	0·562	„
Found in the gas leaving the latter	0·002	„
	100·000	

This, however, only refers to the HCl found by analysis, and takes no account of losses by leakage &c.

According to Schrader (*loc. cit.*), from 92-per-cent. salt as much as 145 parts of acid of 34° to 36° Tw. can be actually obtained, instead of 175·9 parts by theory; according to Payen, 120 to 125 parts instead of 154·7; according to Balard ('Rapport du Jury International,' 1867, vii. p. 45), at Chauny 95 per cent. are recovered, viz. 150 parts acid of 21° Baumé (34° Tw.) to 100 parts salt containing from 5 to 6 per cent. water.

The following statements have been made to the author at German works (1878):—(*a*) 133 parts acid of 21° Baumé (=32° Tw.) from 100 parts of a mixture of 72 rock-salt and 28 nitrecake; (*b*) 140 to 150 parts of acid of 20° Baumé from 100 parts of common salt. The quantity of acid obtained by Jones's mechanical furnace has been stated on p. 106. At Aussig, where the very perfect condensing-apparatus described on p. 242 *et seq.*, and the extremely pure salt of Neu-Stassfurt (which contains 99 per cent. NaCl, and yields 120 per cent. of sulphate) are employed, the very high yield of 148 parts of hydrochloric acid of 34° to 36° Tw. is obtained from 100 parts of *sulphate*.

Purification of Commercial Hydrochloric Acid.

The impurities of crude muriatic acid have been enumerated on p. 179. The *fixed* ones can be removed from the acid in the easiest way by distilling it with the usual precaution of rejecting the first and the last portions of the distillate. Ferric chloride, especially, passes over towards the end of the distillation; nor can it be retained by adding zinc or stannous chloride (to reduce it to $FeCl_2$), but only by the addition of phosphoric acid.

Sulphuric acid can be easily removed by barium chloride; on the large scale most of it can be kept out of the hydrochloric acid by

proper precautions in condensing it. Of course the difficult solubility of $BaCl_2$ in concentrated hydrochloric acid must be borne in mind.

Sulphurous acid and chlorine, according to Domonte, are most easily removed from hydrochloric acid by a current of carbonic acid, without reducing its percentage of HCl. The latter assertion has been refuted by Roscoe and Dittmar, the former by Bolley and Ott, who did not notice the least effect of carbonic acid on the SO_2 contained in muriatic acid (Wagner's Jahresb. 1860, p. 190).

Many proposals have been made for preparing pure hydrochloric acid (free from arsenic especially) from the crude acid. Houzeau (Compt. Rend. lix. p. 1025) states that weak acid can be obtained free from arsenic by simply evaporating it in an open vessel to two thirds of its volume, in which case all the arsenic goes away as $AsCl_3$. In order to obtain a stronger acid, 3 litres of crude acid are put into a 6-litre flask, 0·3 gram of powdered potassium chlorate are added, and the flask is closed by a twice-perforated cork carrying a safety-tube and a wide tube of 20 inches length. The latter is drawn out at the bottom and filled with about 100 grams of copper turnings, and on the top of these with a 3-inch layer of asbestos or pounded glass. This tube projects pretty far into the neck of the flask, in order to be heated by the vapours; its upper end is connected, by another tube, with a receiver containing water. If heat is now applied, by the action of the $KClO_3$, the $AsCl_3$ is converted into non-volatile As_2O_5; the excess of chlorine escapes along with the HCl, but is retained by the moist copper, and drops back into the bottle as a solution of $CuCl_2$. In order that in the boiling liquid an excess of Cl may always be present and the reduction of As_2O_5 be avoided, a current of hydrochloric acid is run in continuously through the safety-tube, containing ten times the original quantity of $KClO_3$. Of course this process is too troublesome and expensive for working on a large scale, and its success is after all only problematical (compare below).

P. W. Hofmann (Deutsch. chem. Ges. Ber. ii. p. 272) found more sulphuric acid in the last receivers of a series than in the first ones, which he attributes to the difficulty of retaining sulphuric anhydride (ought not the gas to be thoroughly moistened?). He, however, made pure hydrochloric acid on a manufacturing scale by running sulphuric acid of 170° Tw. into crude muriatic acid. HCl gas escapes at once, is washed in a washing-bottle, and absorbed in

distilled water. This goes on till the sulphuric acid has got down to 131° Tw. It acts of course by attracting water and driving the free HCl off in the state of gas; it is said to retain only 0·32 per cent. HCl. It may either be employed for decomposing salt or be concentrated. One hundred parts of concentrated oil of vitriol furnish 40 parts pure hydrochloric acid of specific gravity 1·181.

As might be expected, Hofmann's process does not remove any arsenic from the hydrochloric acid, but increases it by that derived from the vitriol. In fact Fresenius found the gas containing arsenic in all stages of its evolution. This, therefore, must in any case be removed in thé first instance.

A suitable plan for eliminating arsenic was proposed by Bettendorf (Dingl. Journ. cxciv. p. 253), viz. adding a solution of stannous chloride in concentrated HCl—which produces a brown precipitate, consisting of arsenic with 1·5 to 4 per cent. of tin, but only in concentrated hydrochloric acid of sp. gr. 1·182 to 1·123: with acid of 1·115 the precipitation is incomplete; with acid of 1·100 no precipitation at all takes place—probably because then the arsenic is not present in the liquid as $AsCl_3$, but as As_2O_3. This reaction is not only very well adapted for detecting arsenic in the presence of antimony, since the latter is not acted upon by $SnCl_2$, but also for purifying crude muriatic acid from arsenic, which is precipitated by a fuming solution of $SnCl_2$, separated by filtration after twenty-four hours, and the acid distilled off almost to dryness: the distillate is quite free from arsenic. Probably, instead of distilling, Hofmann's process of driving out the HCl in the cold by strong vitriol might be employed, if the latter could be obtained free from arsenic.

I. Mayrhofer (Annal. Chem. Pharm. clviii. p. 326) completely confirmed Bettendorf's statements, but found that mere oxidation of $AsCl_3$ to As_2O_5 and subsequent distillation could not purify the hydrochloric acid from arsenic, as H. Rose and others had asserted; for arsenic acid is just decomposed by HCl, especially on heating, with formation of $AsCl_3$ and chlorine, and that all the more easily the more concentrated the HCl.

Hager (Wagner's 'Jahresbericht,' 1872, p. 263) agrees with this, but remarks that, if the precipitate formed in Bettendorf's process is not completely filtered off before distillation, the distillate always contains arsenic, even with an excess of stannous chloride. From the latter stannic chloride is formed

$$(3\,SnCl_2 + 6\,HCl + As_2O_3 = As_2 + 3\,H_2O + 3\,SnCl_4),$$

and passes over into the distillate. Hager consequently recommends the process of Duflos:—The acid is diluted to 1·13 specific gravity; if it contains any SO_2, some MnO_2 (or $KClO_3$) is added; then broad bright strips of copper are put in and digested one day at about 30° C. Then the strips of copper are taken out, scoured, and put into the acid for another twelve or fourteen hours. Thus all the arsenic is precipitated on the copper, the chlorine is removed, and the ferric chloride is reduced to ferrous chloride. Thallium also is precipitated by copper in the presence of arsenious acid. Then the liquid is distilled, after first putting a few scraps of copper into the retort, in order to protect the ferrous chloride against being reconverted into ferric chloride.

Diez accomplishes the same ends by treatmentwith sulphuretted hydrogen, filtering, and distilling (Wagner's Jahresb. 1873, p. 263); Engel (ib. 1873, p. 275), still more simply, by adding 0·4 to 0·5 per cent. potassium hyposulphite, pouring off from the precipitate, and distilling.

Hargreaves and Robinson (English patent dated Aug. 29th, 1872) propose to add the H_2S in the manufacture of HCl on the large scale, before condensation, in order to remove arsenic and to reduce SO_2 to S. The latter is of special importance to them, as in their process the HCl always contains a little SO_2, which is prejudicial in the preparation of chlorine.

The *applications of hydrochloric acid* are extremely numerous. Most of it serves for preserving chlorine, which, in its turn, is employed for manufacturing bleaching-powder and liquor, chlorate of potash, &c., or directly for bleaching. In Germany during the year 1878 the stoppage of several alkali-works raised the price of hydrochloric acid so much that in some places the manufactures of chloride of lime and other applications of that acid at the works themselves have been discontinued.

The applications of *weak* HCl have been described on p. 260. This acid further serves, mostly in its ordinary state of concentration, for preparing the chlorides of zinc, tin, antimony, ammonium, barium, calcium, &c.; for manufacturing bone-glue, superphosphate, purified animal charcoal; for revivifying bone char; for bleaching, partly by itself, partly along with chloride of lime, and in innumerable cases in dyeing and printing; for preparing several other acids, especially carbonic acid (in the manufacture of sodium bicarbonate, mineral waters, &c.); for neutralizing the

caustic soda in manufacturing alizarine and resorcine and in the manufacture of many other artificial colouring-matters; for pickling iron and zinc; for freezing-mixtures (with Glauber's salts and snow); for preparing lead oxychloride from galena by Pattinson's process; for making aqua regia; for purifying sand and clay from iron for glass and ceramic manufactures; for purifying cream of tartar; for precipitating fatty matters from soap-suds, and for decomposing the lime soap formed from the same; for the metallurgical preparation of copper, of galena containing zinc; for getting the zinc from tin-plate scraps; for recovering sulphur from tank-waste; for removing boiler-scale; as auxiliary in diffusion at beetroot-sugar works (Dingl. Journ. ccxxi. p. 92); for saturating the sirups and the manufacture of sugar from molasses by means of alcohol; and for innumerable other purposes.

The *conveyance* of hydrochloric acid mostly takes place in glass carboys, just like that of sulphuric acid, and with the same external packages. More rarely earthenware bottles are used, which must after all be put into baskets for conveyance. Sometimes smaller earthenware bottles, containing about ½ cwt. each, are sent out four together, packed in ordinary packing-cases, this handy kind of packing being required by some consumers. For a considerable time past attempts have been made to replace the fragile glass carboys by gutta-percha vessels; but the expense is against it, since a vessel large enough to hold from 1½ to 2 cwt. of hydrochloric acid, worth, say, two shillings, itself costs £3. This forbids the employment of such vessels, except within a very limited circle around, whence the gutta-percha vessels can be quickly and cheaply returned to the works. According to the most recent publication of Kuhlmann fils, travelling tanks made of hardened india rubber (ebonite) have been found to answer exceedingly well.

THIRD BOOK.

SODA.

CHAPTER I.

HISTORICAL. PROPERTIES. NATURAL SODA.

The compound which now, excepting common salt, is technically the most important of all mineral salts, has not always held this rank, although it seems to have been known from the remotest antiquity. In the Old Testament a substance which served for cleansing, and effervesced with vinegar, is mentioned by the name of "neter." Evidently this was the same Egyptian word which the Greeks rendered by *νίτρον*, the Romans by "nitrum," and which, as we now know for certain, did not signify saltpetre, but soda (Kopp, 'Geschichte der Chemie,' iv. p. 23). The word "natron" is first found in Europe in the 15th century, to denote either the natural alkaline carbonate or that made from plants. The Arabs sometimes called it "nitrum," but more frequently "kali" or "alkali;" even the expression "soda" already occurs in Geber. All three expressions (natron, kali, and soda) meant the same thing, viz. fixed alkali of any kind. What we now call potash and soda, or their salts, were regularly confounded at that time, or taken for mere modifications of the same substance. The first who recognized a difference between them was Stahl, in 1702; but Duhamel, in 1736, first completely established the base of common salt as a peculiar substance, different from that of the "salt of tartar." Still some chemists would not admit any difference between "vegetable" and "mineral" alkali (the latter name had been given to the base of common salt by Marggraf, in 1759). As late as 1782 the Göttingen Society offered a prize with reference to this; but we may consider that the matter was definitely decided about that time (Kopp, *loc. cit.*).

PROPERTIES OF THE CARBONATES OF SODIUM.

Anhydrous sodium carbonate, Na_2CO_3, is composed of

	Molecular weight.	per cent.
Na_2O.........	62·1	58·53
CO_2	44·0	41·47
	106·1	100·00

It is a white, opaque salt, of specific gravity 2·407 at 20° C. (Favre and Valson), 2·6459 (Karsten), 2·509 (Filhol), of 2·509 at 20° and 2·041 on fusing (Quincke). It melts at a moderate red heat, somewhat more easily than potassium carbonate; Carnelly (Journ. Chem. Soc. 1878, ii. p. 280) places its melting-point at 814°, that of K_2CO_3 at 834°. In doing this it always loses a little carbonic acid (viz. at a "yellow heat" 1·34 to 1·38 per cent.); at a "red heat" all the CO_2 is absorbed again except 0·54. On heating by a gas blowpipe the loss of carbonic acid rises to 1·75 per cent., if the salt is in the atmosphere of the products of combustion, rich as these are in carbonic acid; otherwise the loss of CO_2 is proportional to the length of time of heating. Aqueous vapour expels some CO_2 from sodium carbonate melting in a platinum vessel, NaOH being formed. Charcoal at a white heat decomposes it into metallic sodium and carbonic acid. Sulphur acts upon it at 275° C., sodium sulphide and hyposulphite being formed.

It is prepared in the pure state by heating the pure crystallized salt; this, however, is somewhat inconvenient, as the salt first melts in its water of crystallization. It is more conveniently obtained by igniting pure sodium bicarbonate, all the more easily since the latter salt can be readily obtained perfectly pure by washing commercial bicarbonate with distilled water; the crystallized salt is just in this way itself obtained in the easiest manner, by redissolving the calcined pure salt. When brought into contact with water, dry Na_2CO_3 gets heated and then dissolves. It crystallizes from solution with different quantities of water, (1st) according to the temperature of evaporation, and (2ndly) according to whether the solution, prepared at a boiling heat, in cooling down is freely exposed to the air or not. The hydrates are :—

1st. *Monohydrate* (Na_2CO_3, H_2O). Molecular weight 124·1; 85·49 per cent. Na_2CO_3, 14·51 per cent. H_2O. Found in the natural state as *Thermonatrite*. Hardness 1 to 1·5; spec. gravity

1·5 to 1·6. Is precipitated on boiling down an aqueous solution; crystallizes also on the cooling of a saturated aqueous solution above 30° C., or if the decahydrated salt is kept melted some time in its water of crystallization. (According to Thomsen this is dihydrated salt.) It also remains behind when the hydrates richer in water effloresce in the air at 37°·5 C. It forms crystals of the rhombical system, partly of a tabular, partly of a prismatic character. On heating it does not melt, but loses its water between 87° and 100°, and dilapses to a fine powder. In the air it absorbs water and (according to Schindler) carbonic acid. At 104° it is less soluble in water than at 38°. On heating the solution saturated at 38° C. to the boiling-point a portion of the salt is precipitated, and redissolves on cooling in a closed vessel; at 15° or 20° C. this solution contains 52·41 parts Na_2CO_3 to 100 H_2O.

2nd. *Dihydrated* salt (Na_2CO_3, $2H_2O$), according to Thomsen (Deutsch. chem. Ges. Ber. xi. p. 2042), is formed as mentioned above.

3rd. *Trihydrated* salt (Na_2CO_3, $3H_2O$), according to Schickendantz, is found as efflorescences in dry places of the beds of rivers in the Cordilleras. It loses 1 molecule of water on keeping.

4th. *Pentahydrated salt* (Na_2CO_3, $5H_2O$) (with 45·89 per cent. H_2O) is formed from the decahydrated salt on efflorescing in the air at 12½° C.; also, on melting the former salt and pouring off the liquid portion, it crystallizes from the liquid above 33° C.

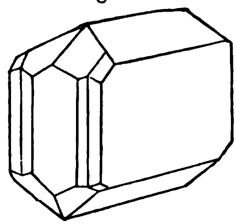
5th. *Hexahydrated salt* has been obtained by Mitscherlich from a solution of Na_2S in the air.

6th. *Heptahydrated salt* (Na_2CO_3, $7H_2O$). Molecular weight 232·1; contains 26·75 Na_2O, 18·96 CO_2, and 54·29 per cent. H_2O. Obtained on melting and slowly cooling the decahydrated salt, or from an aqueous solution saturated while hot, especially if sodium nitrate and chloride are present, but always only if the access of air is restricted, because otherwise the decahydrated salt is formed. It crystallizes, according to Loewel, in two different modifications:—

(*a*) By prolonged boiling of a saturated aqueous solution, crystallizing at 10°–15° C., with restricted access of air and covering the liquid with a layer of previously warmed alcohol, clear transparent rhombohedra are formed, which in the air turn milk-white and become heated, whilst hardening by the crystallization of the enclosed mother liquor to decahydrated salt. This modification is very unstable.

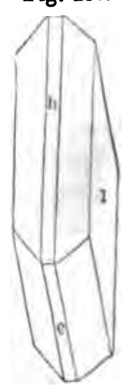
(*b*) The ordinary salt, obtained also by Thomsen, Rammelsberg, and Marignac, crystallizes from soda solutions saturated while hot, on cooling in corked bottles, best of all between 0° and 10° C.—sometimes also in the open air. Rectangular, four-sided plates of the rhombical system, fig. 158, showing many modifying faces on the sides. Spec. gravity 1·51. Does not melt completely on heating; effloresces in dry air and at 30°, or in the presence of oil of vitriol, and leaves monohydrated salt.

Fig. 158.



7th. *Decahydrated salt* (Na_2CO_3, $10H_2O$) forms the ordinary crystal soda as it is obtained both on the small and the manufacturing scale by the cooling of concentrated solutions in the air. Molecular weight 286·1; contains 21·71 per cent. Na_2O, 15·37 per cent. CO_2, 62·92 per cent. H_2O. It is obtained in a pure state from commercial soda crystals by several recrystallizations, the first time adding one thousandth part of lime, which, on being precipitated as carbonate, clarifies the liquid. It is best to disturb the crystallization, because the finely granular salt is more easily separated from the mother liquor containing chloride and sulphate. Ralston obtained from impure soda a pure article by washing with a solution of pure soda. For analytical purposes it is best obtained from bicarbonate, which, owing to its comparatively slight solubility, can be obtained completely free from chloride and sulphate by washing it in the finely granular state with distilled water, and which on being dried and ignited leaves chemically pure Na_2CO_3, from which the decahydrated salt is obtained by dissolving and crystallizing. It forms transparent crystals, as clear as water, of the monoclinic system, fig. 159; the obtuse edge *l* is usually strongly blunted, so that the crystals assume a plate-like habit; more rarely the acute edge *h* is blunted. It is most fissible along *h*, less so along *e*. Different chemists have found its specific gravity from 1·423 to 1·475. It liquefies at 34° C. in its water of crystallization, secreting monohydrated salt and leaving a liquid portion containing upwards of 10 molecules of water, and again solidifying at 33½° C. It effloresces quickly in the air, but not at a temperature of 6° to 12° C. if the dew-point is 2°·8 to 3°·9 below the

Fig. 159.



temperature of the air; at such a state of moisture of the air, on the contrary, anhydrous salt attracts nearly 10 molecules of water in six weeks. If crystal soda effloresces, at 12°·5 pentahydrated, at 38° monohydrated salt remains behind; the latter also in a vacuum beside oil of vitriol, or lime and calcium chloride. When this salt crystallizes out of its solution, so much heat is liberated that the initial temperature of 30° C. remains constant for a long time.

8th. *A salt with* 15 *molecules of water* (Na_2CO_3, $15 H_2O$), containing 71·79 per cent. of water, crystallizes from a saturated solution at −20° C.

Solubility of Sodium Carbonate.

Anhydrous Na_2CO_3 dissolves in water with liberation of heat, decahydrated salt with absorption of heat; on mixing 40 parts of soda crystals with 100 parts of water the temperature is lowered by 9° C., but never below −2° C., because this is the freezing-point of the aqueous solution. The maximum solubility for solutions capable of secreting decahydrated salt (that is, in ordinary circumstances) seems to be at the melting-point of this salt, at 34° C.; above this the solubility decreases. According to Loewel, 100 parts of water dissolve at

0°	10°	15°	20°	25°	30°	38°	104° C.	
6·97	12·06	16·20	21·71	28·50	37·24	51·67	45·47	Na_2CO_3.

corresponding to

21·33	40·94	63·20	92·82	149·13	273·64	1142·17	539·63	Na_2CO_3, $10 H_2O$.

According to Mulder 100 parts of water dissolve at

0°	5°	10°	15°	20°	25°	30°	32°	32°·5 C.	
7·1	9·5	12·6	16·5	21·4	28·0	38·1	46·6	59	Na_2CO_3.

between 34° & 79°	at 80°	85°	90°	95°	100°
46·2	45·9	45·7	45·6	45·4	45·1

The boiling-point of the saturated solution, according to Mulder, is 105°; according to Kremers, 106° C.

The percentage of solutions of sodium carbonate for different specific gravities is as follows.

1st. According to Gerlach; temp. 15° C.:—

Percentage in 100 parts of the solution by weight.	Spec. grav. of the solution for Na_2CO_3.	Spec. grav. of the solution for Na_2CO_3, $10H_2O$.
1	1·01050	1·004
2	1·02101	1·008
3	1·03151	1·012
4	1·04201	1·016
5	1·05255	1·020
6	1·06309	1·023
7	1·07369	1·027
8	1·08430	1·031
9	1·09500	1·035
10	1·10571	1·039
11	1·11655	1·043
12	1·12740	1·047
13	1·13845	1·050
14	1·14950	1·054
15	....	1·058
16	....	1·062
17	....	1·066
18	....	1·070
19	....	1·074
20	....	1·078
21	....	1·082
22	....	1·086
23	....	1·090
24	....	1·094
25	....	1·099
26	....	1·103
27	....	1·106
28	....	1·110
29	....	1·114
30	....	1·119
31	....	1·123
32	....	1·126
33	....	1·130
34	....	1·135
35	....	1·139
36	....	1·143
37	....	1·147
38	....	1·150

2nd. According to Schiff. Temp. 23° C.

Spec. grav.	Per cent. of crystallized salt.	Per cent. of anhydrous salt.	Spec. grav.	Per cent. of crystallized salt.	Per cent. of anhydrous salt.
1·0038	1	0·370	1·1035	26	9·635
1·0076	2	0·747	1·1076	27	10·005
1·0114	3	1·112	1·1117	28	10·376
1·0153	4	1·482	1·1158	29	10·746
1·0192	5	1·853	1·1200	30	11·118
1·0231	6	2·223	1·1242	31	11·488
1·0270	7	2·594	1·1284	32	11·859
1·0309	8	2·965	1·1326	33	12·230
1·0348	9	3·335	1·1368	34	12·600
1·0388	10	3·706	1·1410	35	12·971
1·0428	11	4·076	1·1452	36	13·314
1·0468	12	4·447	1·1494	37	13·712
1·0508	13	4·817	1·1536	38	14·082
1·0548	14	5·188	1·1578	39	14·453
1·0588	15	5·558	1·1620	40	14·824
1·0628	16	5·929	1·1662	41	15·195
1·0668	17	6·299	1·1704	42	15·566
1·0708	18	6·670	1·1746	43	15·936
1·0748	19	7·041	1·1788	44	16·307
1·0789	20	7·412	1·1830	45	16·677
1·0830	21	7·782	1·1873	46	17·048
1·0871	22	8·153	1·1916	47	17·418
1·0912	23	8·523	1·1959	48	17·789
1·0953	24	8·894	1·2002	49	18·159
1·0994	25	9·264	1·2045	50	18·530

3rd. Volumes of the 5, 10, and 15 per cent. solutions of Na_2CO_3 between 0° C. and their boiling-points (Gerlach).

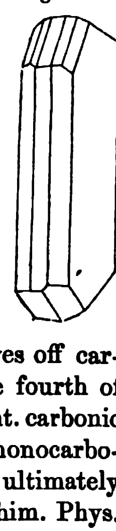
Temperature.	5 per cent.	10 per cent.	15 per cent.
0°	10000	10000	10000
5	10008	10014	10016
10	10018·5	10029	10032·5
15	10031	10045	10051
20	10045	10062	10070
25	10062	10081·5	10090
30	10080	10101	10112
35	10099	10122	10136
40	10119	10144	10160
45	10141	10168	10185
50	10165	10192	10210
55	10191	10220	10236
60	10220	10246	10263
65	10249	10275	10290
70	10278	10304	10318
75	10308	10334	10348
80	10339	10364	10379
85	10370	10395	10409
90	10402	10426	10439
95	10433	10455	10468
100	10464	10488	10499
at boiling-point	10468	10494	10510
Temperature	(100°·5 C.)	(101°·1 C.)	(101°·8 C.)

Sodium sesquicarbonate ($Na_4H_2C_2O_9, 3\,H_2O$). Mol. weight 328·2; contains $2\,Na_2O = 37·85$ per cent., $3\,Co_2 = 40·22$ per cent., $4\,H_2O = 21·93$ per cent. It is found in nature as *trona* or *urao*, and is obtained artificially by quickly boiling down a solution of bicarbonate, so that this loses CO_2, and in other ways. Trona forms transparent brilliant monoclinic prisms; urao is semitransparent, of foliaceous and radiated texture and conchoidal fracture, alkaline, and not efflorescent. The artificial crystals are also stable in the air. Their solubility is between that of monocarbonate and bicarbonate.

Sodium bicarbonate, $NaHCO_3 = CO\begin{smallmatrix} /OH \\ \backslash ONa \end{smallmatrix}$. Molecular weight 168·1; contains 36·94 per cent. Na_2O, 52·36 per cent. CO_2, and 10·70 per cent. H_2O. It is always obtained by the action of CO_2 on ordinary sodium carbonate, and contains nearly always a little of the latter salt; if completely free from it, it does not redden turmeric and does not precipitate a very dilute solution of mercuric chloride, whilst the latter in the presence of monocarbonate gives a red precipitate. The best test, according to Hager, is mercurous chloride (calomel); 0·5 gram Hg_2Cl_2, mixed with 1 gram $NaHCO_3$ and 1·5 gram water, and shaken up, does not blacken in 24 hours in the absence of monocarbonate, but in its presence it turns more or less grey.

The salt occurs in monoclinic tables, usually combined into crusts (fig. 160). It has a somewhat alkaline taste; if entirely free from $NaHCO_3$, it does not change turmeric (as mentioned), but it reddens blue litmus. Specific gravity 2·163 to 2·2208. On ignition it loses water and half of its CO_2, altogether 36·86 per cent., and changes into Na_2CO_3. The crystals remain unchanged in dry air; in damp air they gradually turn opaque and alkaline; the powdered salt, after twelve months' exposure to the air, is converted into sesquicarbonate. If moistened with a little water, the salt loses CO_2 in the air even below 0° C., but the more quickly the higher the temperature, till it has been converted into monocarbonate and dissolved. Its solution in 14 parts of water keeps unchanged in the air; *in vacuo*, however, it constantly gives off carbonic acid and loses 13·94 per cent.—that is, about one fourth of its total CO_2. By long-continued boiling 20·46 per cent. carbonic acid out of its 52·43 are driven off (Rose); ultimately monocarbonate would remain. Already at 70° C. sesquicarbonate is ultimately formed. Its solubility, according to Poggiale (Ann. Chim. Phys. [3] viii. 468), is as follows:—100 parts of water dissolve at

Fig. 160.



0°	10°	20°	30°	40°	50°	60°	70° C.
7·92	8·88	9·84	10·80	11·76	12·72	13·68	14·64 parts.

Both Mulder and Dibbits have pointed out that Poggiale's estimations cannot be reliable, since at 70° C. the compound cannot exist at all.

At 15° C., the tension of the carbonic-acid gas in saturated solutions of the salt is already 120 millims. From his exact estimations, undertaken with special precautions against any loss of CO_2, Dibbits (Journ. prakt. Chemie (2) x. 417) has calculated the following table:—

100 parts of water dissolve							
at	parts $NaHCO_3$.	at	parts $NaHCO_3$.	at	parts $NaHCO_3$.	at	parts $NaHCO_3$.
° C.		° C.		° C.		° C.	
0	6·90	16	9·00	32	11·40	48	14·10
1	7·00	17	9·15	33	11·55	49	14·30
2	7·10	18	9·30	34	11·70	50	14·45
3	7·20	19	9·40	35	11·90	51	14·65
4	7·35	20	9·60	36	12·05	52	14·85
5	7·45	21	9·75	37	12·20	53	15·00
6	7·60	22	9·90	38	12·35	54	15·20
7	7·70	23	10·05	39	12·50	55	15·40
8	7·85	24	10·20	40	12·70	56	15·60
9	8·00	25	10·35	41	12·90	57	15·80
10	8·15	26	10·50	42	13·05	58	16·00
11	8·25	27	10·65	43	13·20	59	16·20
12	8·40	28	10·80	44	13·40	60	16·40
13	8·55	29	10·95	45	13·55	...	...
14	8·70	30	11·10	46	13·75	...	...
15	8·85	31	11·25	47	13·90	...	...

Latterly the fact that sodium bicarbonate is hardly at all soluble in a saturated solution of sodium chloride (or of sodium sulphate, or a mixture of both) has acquired great importance; for the manufacture of soda by the ammonia process is founded upon it.

Natural Occurrence of the Sodium Carbonates.

The sodium carbonates are found widely dispersed in nature, of course containing water and mixed with other salts, as constituents of many minerals, especially of some mineral waters (Aix-la-Chapelle, Karlsbad, Vichy; the Karlsbad springs are said to produce annually 6685 tons Na_2CO_3 and 10,285 tons Na_2SO_4),—further, in the *natron-lakes* of Hungary, Egypt, Central Africa, in

the steppes between the Black Sea and the Caspian, in the large North-American plain between the Alleghanies and the Rocky Mountains, in Mexico, South America, &c.,—also as *efflorescences* (*natron*, *trona*, *urao*) in many places, especially as crusts in the neighbourhood of natron-lakes.

The soda in these cases is derived from various sources—for instance, from the weathering of some minerals and rocks (Kayser found on weathered slate at Clausthal a crust containing 92 per cent. Na_2CO_3—see Liebig's Jahresb. 1850, p. 759), from the action of common salt on limestone (with formation of $CaCl_2$ and Na_2CO_3), from the decay of plants containing organic soda salts, &c. Cloëz (Compt. Rend., June 10th, 1878) considers magnesium bicarbonate a principal agent in the formation of trona &c.; he says that its solution, together with that of sodium chloride, decomposes at the ordinary temperature into $MgCl_2$ and sodium bicarbonate or sesquicarbonate. He, however, appeals only to laboratory experiments, and does not say what becomes of the magnesium chloride.

The water charged with soda salts under favourable conditions collects in ponds and lakes which in summer sometimes dry up entirely and leave the salts as crusts on their bottoms, mostly in a crystalline form, more or less coloured, frequently transparent or semitransparent. In other cases the subsoil moisture is concentrated by evaporation by the heat of the sun in summer time; more moisture is sucked up by capillary action; and thus ultimately efflorescences in greater or less quantity are formed, which frequently contain a good deal of soda.

The oldest known occurrence of natural soda is that in Lower Egypt (d'Arcet, Compt. Rend. Sept. 1845; Landerer, Wagner's Jahresb. 1858, p. 68). There, in the desert near Memphis and Hermopolis, in a valley five miles to the west of the Nile, are nine shallow lakes, ranging from the size of a pond to five miles length by one and a half mile width; the largest, Nehelé, has a depth of 20 feet. These lakes are fed by a large number of small salt springs, which only show $1\frac{1}{2}°$ or $2°$ Tw., whilst the liquid in the lakes themselves shows $48°$ to $52°$ Tw., owing to evaporation by the sun. They are partly coloured red, and contain sodium chloride, sometimes Epsom salts, and but few of them sodium carbonate also. In summer the small lakes dry up entirely, the larger ones on their margins, and leave crusts of salt, mixed with a clayey mud

(*sottanée*). In some of the lakes bottom deposits are said to have gradually formed, whose upper portion, 16 feet thick, consists essentially of NaCl, whilst the lower one, 17 feet thick, contains sodium carbonate. The above-mentioned crusts, which are 15 to 18 inches thick, are pushed off by means of poles and spades, spread out to dry on the banks, and carried in baskets to the Nile, whence the salt is shipped to other parts. It is called "*latroni*" in the Levant and in Greece; the Egyptians use it to soften their very hard drinking-water by precipitating its lime and magnesia salts, the water being afterwards filtered. Its principal use is in Crete for soap-making. Besides sodium carbonate it contains sodium sulphate and chloride, sand, and water. From Alexandria yearly about 2500 tons are exported, on the average at 6 francs 90 centimes per 50 kilograms.

The salt lakes in the Araxes plain in Armenia, in the volcanic region of the Ararat, in connexion with the neighbouring deposits of rock-salt, have been examined chiefly by Abich. There crusts are found both on the bottom and drifting on the water like ice-flakes. Abich states their composition as follows:—

	Lake of Tasch-Burun.	Crusts from the same.	Lake with reddish water.	Crusts from the same.	Flakes from the surface.	Yellow pools without crusts.
Na_2CO_3	0·69	22·91	3·70	16·09	18·42	23·91
Na_2SO_4	0·99	16·05	5·57	80·56	77·44	5·39
NaCl	4·97	51·49	21·36	1·62	1·92	5·38
Mn_2O_3, MgO	...	trace.	...	trace.	trace.	...
Water	93·36	9·88	69·37	0·55	1·18	65·29
	100·01	100·33	100·00	98·82	98·96	99·97

The water of the lake of Wan contains, according to Chancourtois:—

Na_2CO_3	0·861
NaCl	0·938

Na_2SO_4	0·333
K_2SO_4	0·055
$MgCO_3$	0·055
SiO_2	0·018
Fe_2O_3	trace.
H_2O	97·740

Natron-lakes are also found in Persia, Thibet, Tartary, Mongolia, and China.

Rather different from such lake-deposits is the soda occurring as efflorescences on the ground—called in Egypt *trona*, consisting essentially of sodium sesquicarbonate, and of which the following are analyses :—

	Laugier.	Klaproth.	Popp. *a.*	Popp. *b.*	Popp. *c.*
Sodium sesquicarbonate	22·4	32·6	64·3	32·20	26·15
„ sulphate	18·3	20·8	7·5	24·00	66·65
„ chloride	38·6	15	8·4	33·30	2·63
Water	14	31·6	22·5	8·87	4·05
Insoluble	6	...	2·95	1·35	0·40

Remy found in it sodium monocarbonate 18·43, sesquicarbonate 47·29, sulphate 2·15, chloride 8·16, calcium sulphate 0·20, traces of magnesium carbonate, boric acid, and organic substances, insoluble 4·11, water 19·67.

In the oasis of Fezzan in the Sahara there are natron-lakes, of which the largest is 800 metres long and 180 metres wide, and contains islands of solid trona.

The following analyses show its composition :—

	Klaproth.	Joffre (Bull. Soc. Chim. xii. 102).
Na_2O	37·0	39·41
CO_2	38·0	39·58
H_2O and loss	22·5	19·52
Sand	...	0·53
Fe_2O_3	...	0·01
$CaCO_3$	...	0·05
NaCl	...	0·46
Na_2SO_4	2·5	0·44

In Colombia a kind of soda, called *urao*, is obtained from a lake, in which it crystallizes in the hot season, also having the composition of sesquicarbonate, $Na_4C_3O_8+4\,H_2O$. According to Boussingault, Mexican urao contains 41·2 CO_2, 39 Na_2O, 18·8 H_2O, 1 insoluble. A mineral found by him in urao, and called *gaylussite*, consists of 34·5 Na_2CO_3, 33·6 $CaCO_3$, 30·4 H_2O, and 1·5 insoluble (that is, $Na_2CO_3+CaCO_3+5\,H_2O$); it is found in considerable quantities at Lagunilla, near Merida in Maracaibo (Venezuela); the natives call it "clavos," *i. e.* nails, from the form of its crystals. Eighty tons of it are collected there in summer.

In the mud of the Loonar Lake in India (district of Nizzam), there is, formed by drying in summer, a firm white salt, employed for washing and soap-making, which is said to contain 67 per cent. sodium carbonate, 2 per cent. NaCl, and 31 per cent. H_2O. The soda is said to be sesquicarbonate; but Wallace (Chem. News, xxvii. p. 205) found in the soluble portion nearly equal parts of monocarbonate and sesquicarbonate. The following are his analyses of these salt efflorescences :—

	Dulla Khar.	Nummuck Dulla.	Papree.	Bhooskee.
Soluble portion.				
Na_2CO_3*	65·26	7·24	35·61	24·64
CO_2 in excess*	7·35	0·54	3·75	2·25
K_2CO_3	0·27	...	0·13	...
NaCl	0·60	86·66	39·21	20·17
$MgCl_2$	0·67	trace.	trace.	trace.
$CaSO_4$	trace.	trace.	trace.	trace.
Al_2O_3 and $Ca_3(PO_4)_2$	0·50	0·60	0·50	0·30
Insoluble portion.				
$CaCO_3$, $MgCO_3$, Fe_2O_3, Al_2O_3, SiO_2	1·80	1·13	3·95	30·16
Organic substances	0·35	0·23	0·80	2·35
Water of crystallization	23·20	3·60	16·05	20·13
	100·00	100·00	100·00	100·00
* Corresponding to Na_2CO_3	29·85	5·64	17·54	13·80
and $Na_4C_3O_8$	42·76	2·14	21·82	13·09

According to Pfeiffer, a greyish-brown East-Indian soda, giving a brown solution, contained :—

	per cent.
Sand and silica	34·65
Ferric oxide	1·08
Alumina	0·26
Lime	0·16
Magnesia	0·30
Soda, Na_2O	22·59
Potash, K_2O	2·65
Carbon dioxide, CO_2	16·00
Sulphur trioxide	4·01
Chlorine	0·79
Water	17·59
	100·08

Wagner found the alkalimetrical value of an Indian soda =18·3 per cent. Na_2CO_3.

In Arabia there is, on the east coast of the Red Sea, near Aden, a deposit of an amorphous mass, greasy to the touch, of soapy smell, with a crystalline core, which by the Arabians is called *dukduka, hurka,* or *kara,* and is employed mostly for adding strength to snuff, more rarely for washing; it costs 2*s*. per cwt. Haines found in it 51·05 Na_2CO_3, 24·94 NaCl, with traces of Na_2SO_3 and $MgCl_2$, 19·66 water and organic substances, 4·35 sand. He supposes the sodium carbonate to have been formed from seawater by a mutual decomposition of $CaCO_3$ and NaCl (Pharm. Journ. (2) v. p. 226).

Olszewsky found a kind of soda occurring as efflorescence on walls, composed of 20·29 Na_2O, 13·72 CO_2, 60·61 H_2O, and 5·05 insoluble—that is, almost pure decahydrated crystal soda; Ritthausen (Journ. prakt. Chemie, cii. p. 375) found soda of a similar composition.

In North America enormous quantities of alkali are found in lakes and as incrustations in the great desert both east and west of the Rocky Mountains; a portion of this is called Alkali Plain. The Pacific Railway cuts through this district at Laramie (where all the rivers and brooks are saturated with alkaline salts), at Wyoming, and in other places. In California, according to Phillips (Chem. News, xxi. p. 83), a number of lakes are found filling the craters of extinct volcanoes, which are very rich in salts. Lake Owen has

water of sp. gr. 1·076, and contains in a gallon 7128 grains total solids; of this 2942 are NaCl, 956 Na_2SO_4, and 2914 Na_2CO_3. Yellowish-white crusts on its banks contain 2·14 per cent. NaCl, 3·10 Na_2SO_4, 46·10 Na_2CO_3, 0·22 SiO_2, traces of potassium salts, 48·44 water and organic substances.

According to the 'Chemical News' of March 18th, 1870 (xxi. p. 129), two miles north of Sand-Springs Road, 50 miles east of Virginia and Goldhill, an inexhaustible deposit of pure soda was stated to have been discovered; it was said to contain 80 per cent. of pure Na_2CO_3, and to be employed for soap-making, in the metallurgical treatment of ores, and so forth. It was asserted that a million tons of this alkali had been proved by a shaft and a drift; but nothing has since been heard of it.

Pontey (geologist of the Union Pacific Company) describes alkali deposits in the territory of Wyoming, extending over 200 and 310 acres, said to consist of nearly pure sodium carbonate. A deposit of 400 acres is found on the north bank of the Sweetwater in Carbore County, Wyoming, 40 miles from Rawlings (Zeitschr. f. chem. Grossgewerbe, 1877, p. 102).

According to the 'Chemiker-Zeitung,' 1878, p. 345, the proprietors of the soda-lake near Ragtown in Nevada obtain every summer about 300 tons from the water merely by spontaneous evaporation in shallow basins. The raw product obtained is carried to San Francisco, where it fetches about 50 dollars per ton.

The occurrence of natural soda in Hungary has been described in Wagner's Jahresb. 1862, p. 223. It was already known in the times of the Roman dominion as a product of efflorescence on the soil. It is produced by the decay of alkaliferous sand, under the action of lime, water, and air, dissolved in the moisture remaining on the ponds receding; on further evaporation crusts of crude alkali, called székső, are formed on the ground. Few of the ponds themselves contain soda in any considerable quantity; it is even found in places remote from the ponds or above their level. Most of the székső is found in the Debreczin moor between the Danube and the Theiss, south of Kecskemét as far as Szegedin; here alkali containing 70 to 75 per cent. Na_2CO_3 is made from it, whilst further north only a crude article, containing 6 to 15 per cent. Na_2CO_3, is got. The crude salt is lixiviated, boiled down in iron pans by means of straw fuel, melted in the pans, and poured into moulds. It

is generally sent for sale in stony pieces of bluish-white colour; sometimes it is only dried and powdered. In 1852 still 280 tons of 70 to 75 per cent. were made, in 1858 only 150, because the article, with higher wages and dearer fuel and the uncertainty of its composition, could not compete with artificial soda. J. Moser (Liebig's Jahresb. 1859, p. 812) found in 100 parts of székső:—

Na_2O	8·03
K_2O	3·12
CaO	2·72
MgO	trace.
Al_2O_3 and Fe_2O_3	2·33
SO_3	3·48
SiO_2	1·04
H_2O	15·50
Insoluble in NO_3H	54·99
CO_2 and loss	8·79

Schapringer (Dingl. Journ. clxxxix. p. 495) found in two brands of Hungarian soda from Kalocsa:—

	a.	*b.*
Na_2CO_3	28·87	40·25
$NaCl$	31·00	53·93
Na_2SO_4	0·13	0·45
$CaSO_4$	0·39	1·54
Clay and sand	0·41	1·45
H_2O	39·04	2·09
Loss	0·16	0·29

a was a crude product, *b* a "refined" and ground product, at much too high a price for its value.

A specimen of Debreczin soda analyzed by Volland, which contained 89·8 per cent. Na_2CO_3, was, at any rate, far above the average of that article.

Soda from the Ashes of Plants.

Most plants contain, of the two principal alkalies, chiefly potash, and consequently, on burning, furnish crude potassium carbonate. There are, however, certain species to which soda is essential for

their growth; accordingly these are found near salt springs, in salt steppes, and especially on the sea-shore. Down to the end of the last century all the soda of commerce, except trona, was made from the ashes of sea-shore plants. It is remarkable that the plants growing in the sea itself, fucus especially, do not answer this purpose; their ashes, called kelp or varec, contain very little alkaline carbonate, and are not worked on account of this, but for potassium sulphate and chloride and especially for iodine.

The soda-plants proper, growing on the sea-shore and to a certain distance inland, convert the sodium chloride of sea-water, at least partly, into oxalate, tartrate, and other organic soda salts, which on being incinerated yield carbonate. Those growing in Europe belong for the most part to the family Atripliceæ; and the most important are:—*Atriplex portulacoides*; sundry species of *Chenopodium*; *Salsola soda, kali, tragus, arenaria, clavifolia, vermiculata, brachiata*; *Salicornia arenaria, europæa*; *Kochia sedoides*. To other families belong *Statice limonium* (Plumbagineæ) and *Triglochin maritimum* (Junceæ), together with (in warmer climates especially) some Ficoideæ—*Reaumeria, Tetragonia, Nitraria, Mesembryanthemum* (*crystallinum*).

Wherever alkali is made from these plants, they are carefully selected according to the strength of their ashes; the best of them are grown for the purpose. The manufacture of soda from this source used to be carried on on the Scotch and Irish coasts—and, to a much greater extent, has been continued to the present time on the coasts of the Mediterranean, in Sicily, Sardinia (where in 1862, according to Landerer, upwards of 5000 tons per annum were produced), in Spain (especially in the province of Valencia), in Morocco, in Teneriffe,—also in the steppes of South Russia and Armenia. The importance of a proper selection of the plants has been shown by Becker's observations. According to these the richest ashes contain the following percentages of sodium carbonate —*Salsola clavifolia* 45·99, *S. soda* 40·95, *S. kali* 34·00, *S. brachiata* 26·26, *Halicnemum capsicum* 36·79, *Kochia sedoides* 30·84; on the other hand, the ashes of *Schoberia acuminata*, growing in the Russian steppes along with the above species, contain only 7·2 per cent. Na_2CO_3 (Wagner's Jahresb. 1859, p. 155).

The method of obtaining alkali from these plants is very simple. They are collected at a convenient season, dried in the air and sun, and incinerated in pits 1 or 1½ yard square, with paved bottom.

First a fire is made with the driest stock; and it is kept up, by successively putting on more material, for several days without interruption; so that only a small quantity is burnt at a time, and with ready access of air. The ashes collecting, being kept well together in the pit, gradually get up to a red heat and assume a pasty condition, in which they are well worked up with tools; and on cooling they are broken up into large lumps, which are further crushed for sale.

In lieu of the pits, Pellieux and Mazé-Launay employ a furnace, which permits continuous work and utilizing the products of combustion for drying the plants (*Fucus*). Sixty tons of green fucus in 24 hours yield 3 tons of crude alkali (properly speaking, kelp), with an expenditure of 8 or 10 cwt. of coals.

The product made in the pits varies much in colour, mixture with particles of charcoal, &c., according to the treatment and to how the process has been going on. Thus varieties arise even with soda coming from the same place and made in the same way; for instance, in France, the names *soude douce, mélangée, bourde* are used for Spanish soda. The principal descriptions, however, are distinguished by the place of manufacture, which at the same time also determines the manufacturing process and the species of plants employed.

The Spanish soda has always been considered the best; and its special name, "barilla," has been conferred upon all soda made from plants. Even artificial soda was in England first called "British barilla." According to Knapp, the word "barilla" means the plants grown for this purpose (*barilla* or *varilla* in Spanish means brushwood); according to others that name comes from "baril," cask or barrel. This article also goes in the trade by the names of Alicante, Cartagena, and Malaga soda. It consists of firm, fluxed, dark ash-grey or blue-grey masses, containing 25 or 30 per cent. of sodium carbonate. It is hard and difficult to crush, and has a sharp alkaline taste. It is obtained from plants specially grown, which are sown towards the end of the year, harvested in the September following, and then incinerated in the way described. According to Schwarzenberg, p. 266, they are sown in May and gathered in August.

Of the three varieties of Alicante soda the *soude douce* is a well fluxed ash-like mass with 20 to 25 per cent. Na_2CO_3; the *mélangée* a blackish honeycombed mass with sharp fracture; the *bourde* a

low quality, mixed with many particles of coal and containing much common salt and earthy constituents. The Malaga and Cartagena barilla appears in the trade in large, heavy blocks of grey colour, mixed with white, green, and black spots; it contains about 14 per cent. Na_2CO_3.

In the south of France two different qualities are obtained—the "salicor" or Narbonne soda (from *Salicornia annua*) with 14 or 15 per cent. Na_2CO_3, and the "blanquette" or "soude d'Aigues-Mortes" from several other places, made from various other species (*Salicornia europæa, Atriplex portulacoides, A. tragus, A. kali, Statice limonium*) with only 4 to 10 per cent. Na_2CO_3. Still less sodium carbonate is contained in the varec from the north of France, and the Scotch and Irish kelp—which, however, properly speaking, do not count as "soda" at all; but there are several descriptions of varec which contain next to no iodine and all the more sodium carbonate, and kelp was in England and Scotland a source of the latter up to the beginning of this century.

The soda from Teneriffe is the ashes of *Mesembryanthemum crystallinum*; it consists of large, irregular, dark grey lumps, and contains about 20 per cent. Na_2CO_3.

Since vegetable soda or barilla is only fluxed ashes, not purified by lixiviation, it contains all the inorganic constituents of the plants; consequently, on treatment with water, it always yields a large amount of insoluble residue of calcium, magnesium, iron compounds, &c. The portion soluble in water contains, along with sodium and potassium carbonates, the sulphates and chlorides of both alkalies, and a small quantity of alkaline sulphides and hyposulphites, formed by reduction from the sulphates during the incineration. Sometimes common salt is mixed with this soda, as it is alleged, in order to make it more suitable for soap-makers; or, plainly speaking, it is adulterated with salt. Exact analyses are given in the following table.

In 1834 there were still 12,000 tons of barilla imported from Spain into England, in 1850 only 1744 tons, in 1856 2730 tons, and in 1864 1262 tons.

Analyses of Vegetable Soda, according to Girardin (Journ. pr. Chemie, xxxvi. p. 123).

	From Alicante (soude bourde).	Cherbourg (varec).		Villette (varec).	Unknown origin.		Granville (varec).
		a.	b.		a.	b.	
Na_2CO_3	2·00	9·53	3·71	13·76	6·00	6·00	0·22
K_2SO_4	...	22·19	42·54	20·35	18·80	22·00	13·50
KCl	...	16·00	19·64	10·53	...	...	15·60
NaCl	65·00	45·78	25·38	54·11	73·20	68·00	65·68
$CaSO_4$	...	...	...	...	...	...	...
Insoluble	3·00	1·50	0·73	...	...	...	...
Iodine	...	trace.	trace.	trace.	trace.	trace.	trace.
Na_2SO_3	30·00	...	...	...	...	...	...
H_2O	...	5·00	8·00	1·25	2·00	4·00	5·00
Loss	...	...	...	...	...	...	...

CHAPTER II.

HISTORICAL NOTES ON THE MANUFACTURE OF ARTIFICIAL SODA.

All natural soda, including that obtained from plant-ashes, has long since been thrown into the background by artificial soda. We have already mentioned that Duhamel in 1736 first demonstrated with precision the identity of the base of common salt with that of "mineral alkali;" and since that time the problem of manufacturing artificial soda has always remained that of the more or less direct conversion of common salt into sodium carbonate. A few exceptions to this rule will be treated of in their respective places.

Till the time of the French revolution potash was decidedly the most important of the two fixed alkalies. The Arabs had already brought the use of natural soda, appearing as efflorescence, into Spain, whence it had made its way into the rest of Europe; also the other kind of "natural" soda, the "barilla" made from the ashes of some plants, formed an article of trade, and that to a much greater extent than the former; but these two sources were nothing like sufficient to meet the requirements of soap- and glass-making, not to speak of other ways of consuming it, and, moreover, they yielded a very impure product. Potash consequently at that time was much cheaper and was the alkali employed for most purposes. But as at that time and to within a few decades from the present it was obtained exclusively from wood-ashes, it is not at all surprising that the demand, enormously increasing 100 years ago with the development of cotton-spinning and many other branches of industry, could no longer be satisfied from such a stationary source (nay, even steadily decreasing with the progress of civilization) as

the incineration of wood. Least of all could the forests of the industrial nations themselves supply their wants in this respect; and the cost of transit from more woody countries, such as Russia, Illyria, Canada, in the then imperfect state of communication, greatly enhanced the price of the product.

It was therefore very natural that many attempts were made to substitute for potash, steadily increasing in price, the base of common salt, of which, as is well known, inexhaustible sources exist in nature. These endeavours were much stimulated by a prize of 2400 livres, offered by the French Academy of Sciences in 1775 for the solution of the question, Which is the best method of converting common salt into soda? This prize has never, up to the present time, been awarded; nevertheless it certainly gave a most important stimulus to the manufacture of artificial soda, although this "was in the air" and would undoubtedly have arisen, in any case, a little later. To be sure the prize could not be awarded at that time, because none of the processes proposed and partly even practically carried out (for instance those of Malherbe, Guyton de Morveaux, De la Métherie, and others) satisfied the requirement of a practicable manufacturing process, capable of surviving; but from this, more especially from the last-named, the process of Leblanc took its departure, which to this day furnishes the greater portion of the alkali. We shall see this in detail further on.

We will in this place merely point out what a revolution in prices the invention of artificial soda has produced. According to Gossage's 'History of the Soda Manufacture,' p. 24, crystal soda in England, in 1814, cost £60 per ton. It was made already about 1806 by Mr. Losh at Walker-on-Tyne, at first by decomposing common salt with litharge, afterwards (Clapham, 'Soda Manufacture on the Tyne') by decomposition of Russian potash, at £40 per ton, with common salt, to muriate of potash and carbonate of soda, which were separated by crystallization. Having subsequently gone to France and seen Leblanc's process, Mr. Losh introduced the latter into his own works. According to Clapham the price of crystal soda in 1809 amounted to £71. Since about this time kelp with 3 per cent. soda was sold at £11, the above price was not too high; barilla with 25 per cent. soda cost £45 per ton.

In 1824, when Muspratt began to work Leblanc's process, crystal soda was sold at £18 per ton, according to Gossage, or at £29 per

ton, according to Clapham (who quotes the books of the Walker firm); the total production of Great Britain at that time is estimated by Gossage at 100 tons per week, in 1850–60 at 5000 tons per week (probably a little too high); probably it now reaches 8000 tons. The price per ton of crystal soda, on an average of the last ten years, may be stated at £4 10*s*., that of soda-ash at £8; in 1878 the prices were considerably below this.

Interesting notes, but going into too many details for our purpose, on the rise of the English alkali trade are found in Gossage's pamphlet above mentioned, Clapham's 'Account of the Commencement of the Soda Manufacture on the Tyne' (1869), and Mactear's 'Report on the Alkali and Bleaching-Powder Manufacture of the Glasgow district' (1876). Wagner's 'Regesten der Sodafabrikation' (1866) treat the subject in a more general manner. His relation, as well as all other similar ones, is mostly founded upon the Report of a Commission, instituted by the French Academy in 1855, which was to inquire into the claims of Leblanc's descendants to a national reward, published in the 'Comptes Rendus,' xlii. p. 553.

The first claimant of the above-mentioned prize offered by the French Academy, and probably the first who attempted to make soda artificially on an industrial scale*, was the Benedictine Father Malherbe, in 1778. He started from sulphate of soda, which he ignited with metallic iron and charcoal in a reverberatory furnace, and, after cooling, worked for soda by lixiviation. Maquer and Montigny made a favourable report on this process. In the following year (1779) Alban built a factory at Javel, near Paris, to work Malherbe's process; after some years, however, it ceased working, for unknown reasons. Essentially the same was the process patented in 1781 by Dr. Bryan Higgins, in which sulphate of soda was melted with charcoal and then lead or iron was added. This process was taken up again in 1855 by E. Kopp, and at that time excited great, but unfounded, expectations of supplanting Leblanc's process (comp. below).

Next followed Guyton de Morveau and Carny, in 1782, build-

* Scheele had already in 1775 discovered this process of converting common salt into soda by means of litharge, which was subsequently carried out by Lord Dundonald and Losh in England, and has been taken up again quite recently by Bachet; but he himself never made any attempt to utilize that process for manufacturing-purposes.

ing a works at Croisic in Picardy, in which, according to a process discovered by Scheele in 1775, a moistened mixture of common salt and lime was exposed to the air, and after some time an efflorescence of soda appeared on the surface. The factory had to be closed after a very short time for fiscal reasons, consequent upon the salt monopoly; but it would in no case have been able to produce any great results by that process.

Soon after* another proposal was made by De la Métherie. Sulphate of soda was to be ignited with coal, whereby sulphurous acid was to escape and carbonate of soda to remain behind. The ignition was to take place in closed retorts; the escaping sulphurous acid was to be conducted into lead chambers, sulphuric acid made from it, and the latter to be employed for making sulphate from common salt. Undoubtedly this would be an extremely beautiful process if the reactions took place in the manner imagined by De la Métherie; but, unfortunately, on igniting sodium sulphate with coal, much sulphide and but very little carbonate are formed. That this might be "partially" the case, was granted by De la Métherie himself; he proposed to decompose the sulphide (but along with it, of course, any carbonate formed!) by acetic acid or any other organic acid, and to convert the acetate by calcination into carbonate. Impracticable as this proposal manfestly is, it gave to Leblanc, according to his explicit statement, contained in the report of the French Commission, the impetus for his own process; he attained the object, not accomplished by his predecessor, by adding calcium carbonate.

A third factory which was at work already before the outbreak of the French revolution (that is, before Leblanc) was that of Athénas in Paris. There common salt was converted into sulphate, first by means of copperas, afterwards by roasting with pyrites or pyritiferous lignite, and the sulphate was converted into soda by Malherbe's process.

None of the factories erected for the above-mentioned processes could be carried on for any length of time, although the manufacturers wanted neither capital, nor intelligence, nor the advice of the first French chemists; their products could not compete with

* In 1789 according to the report of the French Commissioners; but that is absolutely incompatible with the statement that Leblanc had already in 1787 got the suggestion for his own process from De la Métherie's *published* process.

Spanish barilla either in price or quality, and probably would not be able to do so now, so far as price is concerned. But it was reserved for another Frenchman to entirely accomplish the task propounded.

Nicholas Leblanc, probably the most celebrated name in chemical technology, was born at Issoudun in 1753. About the time when the first above-mentioned alkali-works were founded he was surgeon to the Duke of Orleans (afterwards "Citizen Egalité"), and was even then known as the author of some good papers on crystallization and on chemical subjects. Incited by the prize offered by the Academy, he occupied himself with the problem of making artificial soda; and De la Métherie's impracticable proposal had, as mentioned, suggested to him the proper solution. This is said to have been the case in 1787. In 1789 he proposed to the Duke of Orleans to carry out the new process on a manufacturing scale. Before the Duke agreed to this, he requested the advice of D'Arcet, the professor of chemistry at the Collége de France. D'Arcet got his assistant Dizé to try the process on the small "and on the large scale" under his eyes, and that successfully; he gave a certificate to that effect, dated March 24th, 1790. On the strength of this, at the office of a notary called Lutherland, in London, an agreement was signed (but the agreement is dated Feb. 12th, 1790!), the essential clauses of which are to the following effect. Leblanc undertook to deposit his soda-making process and Dizé a white-lead process invented by him, along with D'Arcet's confirmation of the same, at the notary Brichard's. The Duke of Orleans was to deposit in the hands of his steward Henri Shée the sum of 200,000 livres for the purpose of carrying out the process; and on this sum interest at the rate of 10 per cent. was to be paid out of the first profits. The profits in excess of this were to be divided thus—the Duke to receive $\frac{9}{20}$, Leblanc and Dizé together $\frac{9}{20}$, and Shée $\frac{2}{20}$; but to Leblanc a minimum income of 4000 livres, to Dizé one of 2000 livres was guaranteed.

The specification then deposited at Brichard's was still extant in 1855; the Commission opened it, and found its contents as follows:—Common salt is decomposed by Glauber's process with oil of vitriol, of which about its own weight is required. In order to recover the muriatic acid as much as possible, it can be conducted into ammonia-water, or first condensed and then mixed with the latter. The sulphate is strongly ignited, in order to remove the

last portions of acid, and then powdered. A certain quantity of it is mixed with half of its weight of chalk and a quarter of its weight of charcoal; the whole is finely ground and put into crucibles, which must be only two thirds filled. The crucibles are covered, but not luted, so that the gases may get out; and they are heated first gently, then up to the fluxing of the mass. This melts into a paste, is changed into carbonate of soda, and taken out of the crucibles. The fluxed mass is purified by powdering and boiling with water; from the solution the soda is separated on boiling down, and dried in hot air. Or else the cooled and roughly crushed fluxed mass is allowed to fall to powder in the air, and then washed as above. The calcareous substance and unburnt charcoal are removed by settling and filtering. The ammonia-water is obtained by burning animal substances; the sal-ammoniac is sublimed. The correctness of these statements is confirmed by D'Arcet.

Dizé's description, also extant, only refers to the preparation of lead sulphate from lead nitrate and sulphuric acid; it clearly appears from the documents that he had nothing to do with the invention of the soda-process, and that this exclusively belongs to Leblanc. Dizé, after Leblanc's death, in 1810, and again in 1852, tried to rob him of the inventor's merit; but he was convicted of falsifying the truth already in his lifetime, and, by the Report of that Commission, still more so after his death.

A new agreement of January 27th, 1791, states that the Duke of Orleans is to make over the sum of 200,000 livres to Shée, and that both capital and interest are to be repaid to him by 70 per cent. of the first clear profits. Over and above that, the profits were to be divided in this manner—the Duke to have $\frac{9}{20}$, Leblanc and Dizé together $\frac{9}{20}$, and Shée $\frac{2}{20}$. If the yearly profits should amount to more than a million (that is, 500 per cent. of the capital invested!), the excess over a million was to be divided in a somewhat different way.

On September 25, 1791, upon the report of D'Arcet, Desmarets, and De Servières, Leblanc obtained from the Committee for Agriculture and Commerce of the Assemblée Nationale a patent for his process for fifteen years. The description given therein deserves to be textually reproduced here, as it contains all the essential features of the process, which have remained unchanged up to within a few years:—

"Between iron rollers the following substances are crushed and mixed—

100 lb. of anhydrous sulphate of soda,
100 lb. of pure limestone, or chalk from Meudon,
50 lb. of charcoal.

"The mixture is spread out in a reverberatory furnace, the working-holes are closed, and fire is applied; the substance gets into a pasty condition, froths up, and is converted into soda which is only distinguished from the soda of commerce by a higher strength. The mass must be frequently stirred up during the fusion, for which iron rakes, spatulas, &c. are employed. From the surface of the fluxing mass a large number of flames break forth similar to the flame of a candle. As soon as this phenomenon begins to cease, the operation is finished. The batch is then drawn out of the furnace with iron rakes, and can be collected in any kind of moulds in order to give it the shape of the commercial blocks of soda.

"The operation may also be carried on in closed vessels, such as crucibles, but thereby becomes more costly. The proportions of the raw materials may be changed; for instance, less limestone and coal may be taken; but the above proportions have given the best results. The quantity stated furnishes upwards of 150 lb. of soda.

"The reverberatory furnaces must be built in a durable manner of fire-bricks and bound with iron. The length of the hearth is 6 feet from the fireplace to the chimney [snorehole]; 4 feet 2 in. wide; the arch is very flat, and has a greatest width [?] of 19 inches. As for the rest, such furnaces are universally known."

It will be seen that here all the conditions up to the manufacture of black ash were put so clearly that, with the most moderate skill in building the works, pecuniary success was certain, looking at the comparatively enormous price then paid for soda in the shape of barilla or varec (see above). It appears in fact that the factory erected by Leblanc and Dizé at St. Denis according to the above-quoted agreement, and called "La Franciade," prospered very well; but after a short time every thing was to be lost. Citizen Egalité was arrested in April 1793 by the Comité du salut public, and executed on November 6th of the same year. His

goods, and along with them the works La Franciade, were confiscated, and the contents scattered by public sale. About this time the Comité du salut public, upon the suggestion of Carny, who had a share in the alkali-works at Croisic (see p. 299), resolved that all those carrying on soda-works were bound to deposit all the ways and means for manufacturing soda known to them within twenty days with a special Commission, for the benefit of the State and without regard to any particular advantages or private speculations, in order to cast off the fetters of commercial dependence on foreign nations, and to afford advantages to the fatherland for its means of defence. The Commission consisted of Lelièvre, Pelletier, Giroud, and d'Arcet. This decree was published on the 12th Pluviose of the year II.; and Leblanc and Dizé, whose works had been inventoried four days previously by the municipality, of course at once gave up their process to the Commission. The same was done by Carny himself (who doubtless had convinced himself sufficiently that not much good was to be got by his own process), by Alban (Malherbe's successor), Athénas, and Ribeaucourt (the proprietor of De la Métherie's process). Scheele's process (employing litharge) having been published in the meantime, was added, making the sixth. The official report of the Commission declared the process of Malherbe and Athénas the most economical, especially if pyrites or pyritiferous lignite were employed for converting salt into sulphate, but did not conceal the advantages possessed by Leblanc's process over most others. Although the judgment of the Commission did not hit upon precisely the right thing, it should not be blamed for this. Leblanc's process at that period had not had time to demonstrate its practical superiority to all others; and even very able men, Longmaid and E. Kopp, sixty years later, have reverted to the process then judged the best, although unsuccessfully.

Thus Leblanc and his partners had within a few days lost their works, their patent, and their means, and he was thrown into bitter poverty. It is true that after six years, on the 17th Florial, VIII., the works La Franciade were given up to Leblanc as indemnification for the publication of his patent, and a commission, consisting of Vauquelin and Deyeux, was charged with valuing the damage done to the partnership in order to award compensation. But it was at the end of another six years, on the 17th Brumaire, XIV. (1806), that the Commission made its report; and though

the report was favourable to the partnership, the decision was that the claim against the state was satisfied by the gratuitous handing-over of the works La Franciade.

This was bitter mockery to Leblanc. After the works had been given over to him he had spent all his means in the necessary repairs, and had no working capital left. The small sum of 4000 francs which he received on Fructidor 19th, II., could not do him much good; another sum of 3000 francs, granted on the 9th Ventose, VII., was never paid to him. In spite of an urgent recommendation of the Minister of the Interior to the Minister of Finance, dated 14th Brumaire, VIII., nothing was done for Leblanc, although his merit and the importance to the national industry of carrying on his works were universally acknowledged. As proof of this, on 11th Prairial, XI., the Société d'Encouragement handed over to him its savings of 2000 francs, together with an extremely appreciative address. But these pittances could not, of course, keep up Leblanc for any length of time; they were utterly insufficient for carrying on a factory; the practically negative decision of 1806 deprived him of every hope; and, broken in body and spirit, he ended his life by his own hand in the same year, and in a workhouse. Fifty years later his grandchildren were indemnified by Napoleon III.

The statement of Muspratt (Chemistry, ii. p. 919) that Leblanc had been handsomely rewarded by the English Government is not found anywhere else (the very detailed Report of the French Commission of 1856 on the support given to Leblanc does not give the least hint of it), and seems utterly incredible, especially when we consider what an embittered war was raging between England and France during that period, and, moreover, that Leblanc's process was not introduced into England until a long time after his death. The following sentence in Muspratt, "In Greece and at Rome statues have since been erected to his memory," can, of course, only be regarded as somewhat curiously-worded irony, or else the words "have since been" are a misprint for "would have been." It is well known that neither in Greece nor at Rome do any alkali-works exist.

Muspratt further tries to vindicate for his countryman, the above-mentioned Dr. Bryan Higgins, the merit of having been the inventor of the process, because his patent is dated from July 31, 1781; but here his patriotism has led him astray. Higgins's patent

refers, in the first place, to the manufacture of Glauber's salt. This is to be mixed in certain proportions with charcoal, and heated in a reverberatory furnace until the ignited mass melts and forms mineral alkaline liver of sulphur. Then lead in certain proportions is thrown in; and when it is melted the ingredients are well raked together, and the mineral alkali thus desulphurated floats above the desulphurated lead. In place of lead, other metals may be used, as iron and tin. Another method is, to mix with a strong solution of the liver of sulphur as much argol as will dissolve therein; to this solution powdered chalk is added; the liquor is separated by subsidence and filtration, evaporated to dryness, and the mass calcined. Muspratt concedes that the high price of lead rendered the first-described plan valueless as a commercial process; "but as Higgins states that iron or other metallic oxides" [Higgins says "metals"] "may be used instead of lead, he had clearly developed the principle of Leblanc, who merely replaced the oxide of iron by oxide of calcium or lime; and Higgins, therefore, might be considered the *inventor* of the process." This opinion of Muspratt's is opposed to the following facts:—1st, that Higgins's patent does not speak of oxide of iron, but of metallic iron; 2nd, that evidently he had only worked with lead, and mentioned "iron and tin" merely to "cover the ground;" 3rd, that Malherbe had already, in 1778, employed iron in the same way; 4th, that Leblanc did not employ calcium oxide, but calcium carbonate; 5th, that Leblanc did not first make a liver of sulphur and then throw in lime, as he would have done if he had stood on Higgins's shoulders; 6th, that there is an enormous difference between the patents in every respect. If Dizé has not been able to snatch the honour of the invention from Leblanc, Bryan Higgins is even a less formidable rival.

As to the rest, only one day after Higgins the same process was patented to A. Fordyce, who, besides iron, mentions calx of iron also.

The working of Leblanc's process was not put an end to by his death. Already in the same year an alkali-works was founded in Paris by Payen, another by Carny at Dieuze; and within the twelvemonth the St.-Gobain plate-glass works exhibited glass plates made with Leblanc's soda. From that time the soda-manufacture developed rapidly in several parts of France, as in the north, near Rouen, at Chauny, near St. Gobain, in the south at Alais and Marseilles, in

the east at Thann near Mulhouse (the latter now in German Alsace). In England Leblanc's process was introduced by W. S. Losh, who had seen it in operation at Paris; but on his return to England he did not in the first instance introduce this process, but Scheele's litharge process (in 1806), at his works at Walker-on-Tyne, where a weak brine spring gave the first impulse to the manufacture. Even later on, all sorts of other plans were tried there: for instance, Russian potash was decomposed with brine, according to Lord Dundonald's patent. About the same time (1803 to 1818), at St. Rollox, soda was made from the chlorine still-liquors, which contained sodium sulphate and chloride along with manganese chloride, by calcining with coal-dust and lixiviating with addition of quick lime. It appears that Losh carried out Leblanc's process for the first time in England in 1814 (that is, twenty years after the inventor), and on a very small scale: ½ cwt. of sulphate was fluxed with slaked lime and coal into balls. In 1820 the charges were increased to 1 cwt. Already in 1816 the firm of Tennants at St. Rollox had some correspondence with Chaptal and d'Arcet on Leblanc's process, and in 1818 definitively introduced it (Mactear, p. 25); and at the end of the year they sold crystal soda at £42 per ton. In the same year 100 tons, in 1829 1400 tons, in 1876 14,000 tons were made there. In 1820 potassium carbonate was also made there, and sold at only £15 per ton, which proves the enormous revolution in price between that and the present time. Soda ash was first made at St. Rollox in 1833, and sold at £22 per ton (against £12 for soda crystals); in 1865 12,500 tons of this article was manufactured there.

The introduction of Leblanc's process on a really large scale into England took place on the abolition of the enormous duty on salt (which amounted to £30 per ton). It was carried out by James Muspratt in 1824. At first the soap-makers would not buy the new soda, because it was so different from barilla and kelp (that is, much purer and stronger); Muspratt had to give away large quantities of it to overcome that prejudice. Of course this was soon effected; and in order to satisfy the overwhelming demand the crude soda had to be delivered to the buyers straight from the furnaces, hardly cool enough to be handled. For six years Muspratt's works remained the only one in England, except a few small works on the Tyne. The increase which has taken place in alkali-making in Great Britain since is well known; it is almost entirely con-

centrated in the two districts of South Lancashire and Tyneside, apart from a few works in Scotland, in the midland counties, and several works in Ireland only going as far as sulphate.

In Germany the first Leblanc soda was made at the works of Hermann and Sons at Schönebeck, near Magdeburg, at which, however, in 1843, not much over 200 tons per annum was made. At a pretty early date a second small works was established at Ringkuhl, near Cassel. During the last twenty years a great number of alkali-works have sprung up in that country, but not sufficient to cover its own consumption, which is made too difficult by the English competition.

In Austria the first alkali-works was erected in 1851 at Hruschau in Moravia, a second one at Petrowitz in Silesia; the largest Austrian alkali-works, and one of the finest of all, that at Aussig, was erected in 1856 under the management of Max Schaffner.

Leblanc's process is in principle substantially carried out everywhere in the way its inventor has indicated. The enormous changes which the factories have undergone in the course of time are chiefly confined to the apparatus. Not to speak of the improvements in vitriol-making, which has been developed almost exclusively in connexion with alkali-making, the principal landmarks in the history of the manufacture of sulphate and of alkali itself are:—the enlargement of soda-furnaces by d'Arcet; Gossage's coke-towers for condensing hydrochloric acid; Gamble's and Lee's decomposing-pans; the rational system of lixiviation, formerly ascribed to Shanks; the manufacture of caustic soda, essentially due to Gossage; the introduction of revolving ball-furnaces, due to Stevenson and Williamson; the general introduction of mechanical power in the whole manufacture (for instance, Mactear's carbonating furnace); the regeneration of sulphur from the tank-waste, by Schaffner and Mond. We purposely omit mention of those improvements introduced during the last few years whose value is still under discussion.

Leblanc's alkali-making process must to this day be called the general though not the universal process. It certainly is not theoretically perfect; but its greatest and almost its only *essential* drawback is that the sulphur entering into the process is partly, in most works entirely, lost, producing a very disagreeable waste product (unless the invention just patented of Schaffner and Helbig for utilizing alkali-waste, to be described in the chapter on that

subject, should remedy this); further, the roundabout way through sulphuric acid and sulphate undoubtedly involves much expense for plant and working and a good deal of complication. The formation of hydrochloric acid as a by-product, which formerly in some places might be regarded as the most formidable drawback connected with Leblanc's process, has now-a-days in many places become the most profitable part of the manufacture, partly directly, partly by the manufacture of bleaching-powder and chlorate of potash. But of the soda itself a good deal is lost, in the most favourable case 14 per cent.; and in many (but not in the best) works that which is obtained is somewhat impure.

The drawbacks just mentioned explain why a great number of proposals have been made for replacing Leblanc's process by a better one; mostly the avoidance of the loss of sulphur was the primary aim. But of all these proposals, ingenious as many of them are, only one has proved its vitality, viz. the so-called ammonia process, as we shall see hereafter; and even this process, extremely successful as it has proved in some places and under special circumstances, does not as yet show any signs of supplanting Leblanc's process otherwise than in special circumstances—for instance, near abundant brine-springs &c., where very pure soda is wanted, where ammonia is cheap, and so forth. The cryolite process also continues to exist, but, owing to the extremely restricted occurrence of that mineral, cannot possibly extend any further. The non-vitality of Kopp's process, which is still quoted as a hopeful one in the most modern treatises, was demonstrated twenty years ago (see below).

CHAPTER III.

SYNOPSIS OF THE VARIOUS PLANS PROPOSED FOR MANUFACTURING SODA.

In the following the various methods for manufacturing artificial soda will be enumerated in systematical order, without regard to the chronological succession of the inventions, or of their degree of practicability; but an opinion upon the latter in some cases will be given, where there are grounds to go upon. In order to avoid separating kindred matters, the proposals for direct production of caustic soda will be enumerated as well as those for producing sodium carbonate.

Our primary divisions, like those of all other authors, are founded on the soda-containing minerals which serve as raw materials for the processes proposed. These are:—

I. Common salt (*i. e.* direct, without being converted into sulphate).

II. Sodium sulphate.

III. Cryolite.

IV. Sodium nitrate.

V. Soda-felspar.

I. Soda direct from Common Salt.

1. *By means of potash.*—Bergmann seems to have been the first who proved that a solution of common salt can be decomposed by potash, and who found that, on evaporating a mixed solution, first a crop of potassium chloride and then one of sodium carbonate are obtained. The first explicit description of this process was given by the Court-apothecary Meyer at Stettin, in 1784. The same plan was recommended by Samuel Hahnemann, Wiegleb and Westrumb, Kastelleyn and Remler (Wagner's 'Regesten,' p. 16). In England Losh manufactured soda at Walker-on-Tyne from 1802

to 1815 according to Lord Dundonald's patent of 1795, in this way:—Equal parts by weight of Russian potash, at £40 per ton, and common salt were dried in a furnace, mixed with slaked lime and small coal and melted in a reverberatory furnace. The product was lixiviated and boiled down until, on cooling, a crop of potassium chloride could be obtained. After a second crop of the same had been separated, the mother liquor was evaporated to dryness, the residue ignited and dissolved for making soda crystals. From 40 cwt. of a mixture of salt and potash 20 cwt. of potassium chloride and 20 cwt. of "British ash" were obtained, or, instead of the latter, 30 to 40 cwt. of crystal soda. The "British ash" was sold at from £16 to £20 per ton, the crystal soda as "potash-soda." The crystallization took place in small shallow lead vessels, only during the winter months (Clapham, *l. c.* p. 8).

To this category also belongs the process of Bischof of Lausanne (Dingl. Journ. iv. p. 380), who tried to make sodium bicarbonate by passing carbonic acid gas into an aqueous solution of equal parts of potash and common salt: sodium bicarbonate was separated; and potassium chloride remained in the mother liquor.

It is hardly necessary to mention that with the present relation of the prices of potash and soda such processes are entirely out of the question.

2. *By means of lime* (Wagner's 'Regesten,' p. 16).—Scheele, in 1773, noticed that from a damp mixture of common salt and lime soda effloresces in the air after several weeks' time. Probably independently of Scheele, this observation was also made by the French chemists Proust, Pelletier, and Deyeux. On the strength of the latter, Guyton-Morveaux and Carny, in 1782, obtained a French patent for soda-making which was actually worked for some time, but with little success, at Croisic in Picardy (comp. p. 299).

From a solution of common salt a solution of calcium bicarbonate precipitates sodium bicarbonate. Apparently this reaction explains the formation of soda efflorescences in soils containing common salt.

3. *By means of lead oxide.*—In 1773, Scheele noticed that common salt is decomposed by litharge. A solution of common salt, filtered through a layer of litharge, became caustic, and in the air yielded carbonate. The reaction is as follows:

$$2\,NaCl + 2\,PbO + H_2O = 2\,NaOH + \begin{matrix} Pb-Cl \\ \rangle\,O \\ Pb-Cl \end{matrix}$$

This observation was published by Bergman in 1775. Kirwan reports that soda was made in England by this process already in 1782, and the yellow residue (of lead oxychloride) was employed as a pigment. The latter was patented as the principal thing in 1787 by Turner, and has retained the name of Turner's yellow ever since; the caustic soda was only a by-product in this case. Göttling (1781) and Achard (1784) knew the process and pronounced against it. In 1792 it was patented in France in the name of Curandau; and it emerges again in 1793 in the report of the Comité du salut public as the process of Chaptal and Bérard, who had favourably judged of it. We have already mentioned that this was the process first employed by Losh at Walker. There 50 parts of finely ground litharge was gradually mixed with 12½ parts of common salt dissolved in 55 parts of water, always leaving the mixture at rest for some hours, till a white crust had formed; this was first broken up and mixed with the mass before new brine was added. After two or three days the batch was finished; the caustic soda was lixiviated with water and the yellow residue melted and sold as a pigment; or, as this could not always be done, the lead was smelted from it again at considerable loss. According to Clapham (Chem. News, xxi. p. 148), by this process, in the *best* case, only 5·6 per cent. of the salt was decomposed, which only with the then very high price of salt could leave any margin of profit. The patent of Watt and Tebbutt, of Jan. 11, 1838, quotes this process again, but prescribes boiling the lead oxide and common salt together. A patent of J. Hunt's (May 7, 1839), if it has any meaning whatever, belongs here. According to it, common salt was to be ground up with granulated metallic lead or zinc. Anthon, of Prague, pronounced a favourable opinion of the litharge process, on the strength of experiments on the small scale. In 1866 (Aug. 14th) Rowbotham obtained provisional protection for the original process of Scheele; but the matter was first taken up again seriously in 1869, by Bachet, whose process was tried in 1870, on a pretty large scale, at the same Walker works which had formerly belonged to Losh. This trial, however, was soon discontinued. The principal difference of Bachet's process from the previous one consisted in his adding slaked lime: 5 cwt. of a mixture of 100 litharge, 70 common salt, and 50 slaked lime was ground in a mill with a little water. Decomposition sets in at once; caustic soda, lead chloride, and hydrated lead oxide (which, it is remarkable, does not act on salt) are generated; but only 19 to 20 per cent. of the salt is decomposed.

The white pasty mass is strongly pressed; and the clear solution of caustic soda and common salt that runs off is ground with fresh quantities of slaked lime and lead oxide. Thus gradually 47 to 50 per cent. of the salt can be converted into caustic soda. The solution pressed off at last is filtered through a layer of calcium hydrate in order to deprive it of any dissolved lead compounds, and concentrated by evaporation, during which the greater part of the NaCl is separated and can be fished out. Caustic soda with 70 per cent. Na_2O could thus be produced. The chief thing, however, has still to be mentioned, viz. the regeneration of the lead oxide; and upon this the process was wrecked. The cakes of $PbCl_2$, $Pb(OH)_2$, unchanged PbO, and $Ca(OH)_2$ remaining in the press were first heated to 173° C. in order to convert the $Pb(OH)_2$ into PbO; and the mass was then introduced into boiling lime-water, in which the $PbCl_2$ also was transformed into PbO; the residue was again employed for decomposing common salt. The filtrate could be almost entirely deprived of the lead which it still contained by cooling and crystallizing, followed by addition of common salt. But apart from the fact that this regeneration could not be carried out without a considerable loss of lead, the recovered lead oxide frequently proved much less active than fresh litharge—probably because much calcium and lead carbonate was formed, which not only are inactive towards common salt, but even seem to interfere with the action of lead oxide. After prolonged trials, the process had to be given up as useless (Chem. News, xxi. p. 148).

Zinc oxide has been proposed for the same object, but without any better success.

The litharge process has been taken up again in a recent patent by Knab (Aug. 13th, 1877, No. 3082). Common salt is to be mixed with its equivalent of litharge; five times its weight of water is to be added, and the heat raised by means of steam to 70° or 80° C. In a few hours the decomposition is complete. The mass is deprived of the largest portion of its caustic soda by hydraulic pressure, and the remainder of the soda obtained by stirring up the lead chloride with water and repeatedly pressing it. The $PbCl_2$ is instantaneously decomposed by stirring up with its equivalent of ammonium carbonate and water, a solution of sal-ammoniac and lead carbonate being formed. The latter is sold as such, or reconverted into PbO by ignition, whilst the CO_2 given off, along with the NH_3 evolved from the sal-ammoniac, again forms ammonium carbonate. In order not to lose the chlorine, the sal-ammo-

niac is not decomposed by lime, but by manganese protoxide, NH_3 and $MnCl_2$ being formed. The latter by heating with access of air is converted into Mn_2O_3, Cl becoming free. As the Mn_2O_3 does not decompose NH_4Cl, it is reconverted into MnO by heating with sulphur, SO_2 being formed at the same time.—This process, extremely complicated in its last part, is founded upon reactions several of which have long been proved extremely incomplete, and consequently has no technical value whatever.

4. *By means of lead or zinc pyrophosphate.*—Margueritte, on Dec. 22nd, 1854, patented the following process. NaCl is heated with lead or zinc pyrophosphate ($Pb_2P_2O_7$ or $Zn_2P_2O_7$). Sodium pyrophosphate is formed, which remains behind, whilst $PbCl_2$ or $ZnCl_2$ is volatilized and condensed in chambers. The sodium salt, dissolved in water and boiled with lime, yields a solution of NaOH and a precipitate of $Ca_2P_2O_7$. The precipitate is again boiled with the previously condensed metallic chlorides, and yields a solution of $CaCl_2$, which is run to waste, along with a precipitate of lead or zinc pyrophosphate, which is again employed for decomposing. The caustic soda can, if required, be converted into carbonate by a current of carbon dioxide (!).

5. *By means of sodium phosphate.*—Arrott (patent of Aug. 16th, 1872) dissolves trisodium phosphate (Na_3PO_4) in water, and treats it with CO_2 or $NaHCO_3$; disodium phosphate (Na_2HPO_4) and Na_2CO_3 are formed, and separated by fractional crystallization. The Na_2HPO_4 is again converted into Na_3PO_4 by melting two equivalents with a little more than one equivalent of NaCl. On June 27th, 1873, Arrott obtained provisional protection for a process of making soda-ash and chlorine by igniting ferric phosphate with common salt, with the assistance of air and steam. The HCl escaping is condensed as usual; the residue contains Fe_2O_3 and sodium phosphate, which is dissolved out and decomposed by lime into caustic soda and calcium phosphate; the latter serves for again producing ferric phosphate with the Fe_2O_3 dissolved in the hydrochloric acid. Criticism of these proposals seems quite unnecessary.

6. *By means of sodium metaphosphate* (according to Siebel, Deutsch. chem. Ges. Ber. viii. 1786).—Sodium metaphosphate is melted with sufficient $NaNO_3$ in a retort-like vessel, so that along with escaping nitric acid, which is condensed as usual, a basic salt is formed; this is treated with a little water, afterwards with CO_2; sodium carbonate and phosphate are formed, dissolved out, evapo-

rated to 77° Tw.; a concentrated solution of ammonium carbonate is added, the whole allowed to cool, and the microcosmic salt, $Na(NH_4)HPO_4$, crystallized out. Thus about two thirds of the soda remains in solution as carbonate, along with a little microcosmic salt. CO_2 is passed through the solution, whereupon $NaHCO_3$ is precipitated; the mother liquor is added on dissolving the next bath of basic sodium phosphate. The microcosmic salt is pressed off and heated, the NH_3 volatilizing is again worked up for ammonium carbonate, and the remaining metaphosphate employed as above. The inventor of this remarkably complicated and unpractical-looking proposal sees no essential difficulty in it, except the selection of a suitable material for the vessels, as which he proposes plumbago.

7. *By means of magnesia and carbonic acid* (Weldon's patent of March 1st, 1866).—A mixture of common salt, cold water, and magnesia or magnesium carbonate is saturated with carbonic acid under pressure in a closed vessel, with or without agitation. Soluble magnesium bicarbonate is formed, which at once decomposes its equivalent of NaCl, $MgCl_2$ being formed and remaining in solution, whilst $NaHCO_3$ is precipitated. The solution of $MgCl_2$ is evaporated to dryness, the residue ignited, the HCl driven off and condensed, and the MgO recovered for use. The $NaHCO_3$ is calcined so as to obtain Na_2CO_3. Weldon expected the hydrochloric acid generated to cover all expenses, and to obtain the soda gratis. The reaction would be:—

$$2\,NaCl + MgCO_3 + CO_2 + H_2O = 2\,NaHCO_3 + MgCl_2.$$

Wagner (Jahresb. 1873, p. 256) points out justly that this process is the most perfect of all soda-making processes; it would be better to say "would be" the most perfect, if all the reactions went on as smoothly as in the equation; but this is evidently not the case, as the process has not been applied in practice. It seems to deserve closer investigation.

8. *By means of oxalic acid.*—Kobell (Wagner's 'Regesten,' p. 18) proved that sodium chloride can be converted into carbonate by oxalic acid on ignition, CO and HCl escaping. But, looking at the high price of oxalic acid, only those processes can claim a technical interest which recover that acid. All endeavours in this direction are founded upon the slight solubility of acid sodium oxalate in water, and are carried out by adding to a concentrated solution of salt an excess of oxalic acid, so that the acid oxalate,

$C_2HNaO_4 + H_2O$, is precipitated and HCl remains in solution. The precipitate is converted into caustic soda and calcium oxalate by boiling with milk of lime, and the oxalic acid recovered from the latter by sulphuric acid. This process was patented by Samuel on Nov. 13th, 1838, again by Margueritte on Jan. 20th, 1855, and by Weldon on March 1st, 1866, but with the addition that the hydrosodic oxalate was to be boiled with quicklime or calcium carbonate. The latter does not answer the purpose, as Anthon and R. Wagner have found ('Regesten,' p. 18). Only half of the oxalic acid is precipitated by $CaCO_3$, the other half remaining dissolved as $C_2Na_2O_4$; but a mixture of milk of lime and chalk, or the latter by itself (as proposed by Samuel) fulfils the intention. The process is not practicable, because much oxalic acid is lost, its recovery is not easy, and its price is high. On Nov. 16th, 1864, Newton (for Bang) patented the decomposition of NaCl with *ammonium oxalate* in hot concentrated solutions; NH_4Cl remains dissolved, $NaHC_2O_4$ falls down, is isolated by decantation, washed with a cold concentrated solution of pure $NaHC_2O_4$, decomposed by CaO into NaOH and CaC_2O_4, and the latter converted by NH_3 (from the NH_4Cl) and CO_2 into $CaCO_3$ and $(NH_4)_2C_2O_4$. (This patent did not get beyond the stage of provisional protection.) Knab obtained a French patent (Jan. 3, 1877) for exactly the same process.

9. *By means of magnesium oxalate.*—Bohlig (Dingl. Journ. ccxxiv. p. 621), 1st, mixes magnesium oxalate, common salt, and hydrochloric acid cold, and lets the mixture stand. A crystalline precipitate of $NaHC_2O_4$ and a sirupy solution of $MgCl_2$ are obtained, according to the equation

$$MgC_2O_4 + HCl + NaCl = NaHC_2O_4 + MgCl_2.$$

The solution of $MgCl_2$ is displaced by water; and as it contains an excess of HCl, it is used over again till it is saturated. 2nd. The $NaHC_2O_4$, by agitation with $MgCO_3$ and water at a pressure of two atmospheres, is converted into a coarse crystalline precipitate of MgC_2O_4 and a concentrated solution of $NaHCO_3$. 3rd. The latter, by boiling with magnesia, is converted into a solution of Na_2CO_3 and $MgCO_3$. Thus one half of the $MgCO_3$ required in the second stage is obtained; the other half is obtained by treating the MgO formed in the 4th stage with fire-gases. The solution of soda contains a little sodium oxalate, which on concentration to 77° B. and cooling is completely precipitated. 4th. The solution of $MgCl_2$ is boiled down, and by heating decomposed

into MgO and HCl. 5th. The oxalic acid intended for replacing that which has been lost is prepared by heating caustic potash with sawdust to dryness, melting, lixiviating, recrystallizing the potassium oxalate, and precipitating MgC_2O_4 by means of $MgCl_2$ or $MgSO_4$. Pure oxalic acid can be obtained by treating the magnesium oxalate with HCl. The principal weak points of this rather ingeniously combined proposal seem to be, 1st, the difficulty of completely decomposing the $MgCl_2$, and, 2nd, the expense of replacing the oxalic acid lost.

10. *By means of hydrofluoric acid.*—Weldon's patent of March 1st, 1866, prescribes decomposition of NaCl by HFl into NaFl, boiling this with MgO, and decomposing the $MgFl_2$ by SO_4H_2. NaFl may also be decomposed by CaO, $CaCO_3$, or steam. The details will be given further on, when treating of the employment of HFl with sulphate. NaCl (according to him) can only be partly decomposed, if precipitated from a saturated solution by aqueous HFl, but much more completely if cooled HFl gas is passed in a moderately quick current into NaCl solution. Spilsbury and Maugham had already, in 1837, proposed the use of HFl (see below).

11. *By means of hydrofluosilicic acid.*—Spilsbury and Maugham on February 6th, 1837, patented the following precess:—A solution of common salt is mixed with hydrofluoric, or, better, with hydrofluosilicic acid, and the precipitate of Na_2SiFl_6, by boiling with milk of lime, converted into NaOH and $CaSiFl_6$. Anthon tried this process in 1840, and obtained good results (Wagner's Jahresb. 1863, p. 228); but the difficulty of washing such a voluminous precipitate was not taken into account. A similar process was patented on March 2nd, 1858, by Newton for Le Chatelier, and in 1858 by Kessler in France; an English patent, Gattmann's (1868), also belongs here. Hydrofluosilicic acid is prepared by melting a mixture of sand, clay, and fluorspar and condensing the vapours; this is employed for decomposing a solution of common salt. The precipitated Na_2SiFl_6 is decomposed by ignition into NaFl, and this, by boiling with chalk, into Na_2CO_3 and $CaFl_2$. The latter is mixed with the HCl and gelatinous silica formed in the previous stages of the process, also with common salt; thus again Na_2SiFl_6 is formed, and so forth (Hofmann, 'Report by the Juries,' 1863, p. 30).

Whether this process could ever pay, would depend to a great extent on the cheap production of hydrofluosilicic acid. In 1865

E. Karcher and Tessié du Motay patented in France the production of that acid (or, in the first instance, of $SiFl_4$) by igniting a mixture of sand, fluorspar, and coal. (Former trials in that direction by Bredberg and Berthier are mentioned in Wagner's 'Regesten,' p. 20.) Fluorspar (Biedermann, in Hofmann's 'Bericht,' 1873, i. p. 316), silica, and clay were mixed in such proportions that a good slag could be formed and moulded with addition of coal into bricks, which were dried and smelted with coke in a blast-furnace of 33 to 40 feet height. The slag contained calcium silicates and still 15 to 20 per cent. $CaFl_2$. The gases given off, consisting of $SiFl_4$, N, CO, and CO_2, were collected at the mouth, and carried to five large wooden condensing-vessels in which slanting glass plates were placed and constantly kept wet. At the bottom of the vessels silica was deposited, and a solution of H_2SiFl_6 was formed; the latter was methodically conducted from one of the condensers to another. An agitator, causing a finely divided spray of water, would probably replace the glass plates with advantage. It is not easy to produce acid beyond 1·072 sp. gr. = 9 per cent. H_2SiFl_6; for technical purposes half that strength would suffice. The latter costs at least 2 francs per kilog.; 100 litres of it are equivalent to 9 kilog. chamber-acid (of vitriol-chambers).

A factory, working by this plan and managed by F. Bothe, existed till 1870 at Grossblittersdorf near Saargemünd, but was not started again after the war, because several serious drawbacks had appeared. The decomposition of $SiFl_4$ by water was not perfect; a good deal of it escaped and caused complaints on account of nuisance. In spite of an excess of silica, HFl was always formed as well, and caused great trouble in decomposing the salt. Worst of all was the fact that sodium fluosilicate is only very imperfectly decomposed into silicium fluoride and sodium fluoride by ignition, even after twenty-four hours' most intense heating, both with compressed and exhausted air. For these reasons the process was discontinued.

12. *By means of alumina.*—Tilghman on February 1st, 1847, patented, among other things, a process for making soda from common salt (or sulphate) by the assistance of alumina. The latter, made by heating aluminium sulphate, was to be filled in pieces of about ¼ cwt. each into a red-hot cylinder of fireclay with a magnesia lining, and vapours of common salt mixed with steam passed into it. The latter are obtained by admitting steam into a cast-iron retort in which common salt is kept in igneous fusion.

The reaction takes place thus:—

$$Al_2O_3 + 2NaCl + H_2O = Na_2Al_2O_4 + 2HCl.$$

(We employ this formula for sodium aluminate merely for the sake of simplicity; probably different compounds, up to $Na_6Al_2O_6$, are formed.) Besides, strongly superheated steam is directly admitted into the apparatus, which must be strongly red-hot or white-hot. By a test-hole in the exit-pipe the quantity of steam is controlled; there ought to be little salt and much acid found in the gases. On the one hand, HCl is formed, and condensed by suitable apparatus; on the other hand, a mass containing sodium aluminate remains behind in the retort. This is lixiviated with hot water, the residue dried and used over again; the solution is treated with CO_2, by which aluminium hydrate is precipitated, whilst sodium carbonate remains in solution and can be obtained by crystallizing &c. (exactly as in the manufacture of soda from cryolite, Chapter XVII.). When the process was carried out at Glasgow on a large scale, the impracticability of introducing common salt in this way must have become apparent; for there a paste was made from alumina and salt, formed into small hollow cylinders of 4 inches length and 1 or 2 inches diameter, dried sharply, and the decomposing-cylinder filled with them. They were finally got back without change of form, containing *partly* sodium aluminate, and were moistened with water and exposed to a current of CO_2 and steam. On lixiviating, soda was obtained and alumina remained behind. Knapp (Liebig's Jahresb. 1847–48, p. 1052) states that the reaction of Al_2O_3 on NaCl at a red heat is not very energetic; and the necessity of employing a white heat is very troublesome in practice. In Glasgow, in fact, only 32 per cent. of soda was obtained, and great difficulties were experienced in treating and recovering the light flocculent alumina—a difficulty attaching to all soda-making processes which employ alumina or silica. These facts, no doubt, were soon recognized after the publication of the process (which had awakened much interest); for the matter went to rest, till a cheaper and handier source of alumina was found in *bauxite*, a natural aluminium hydrate containing ferric oxide. Lechatellier and Jacquemart were the first who employed this mineral for preparing sodium aluminate, in the aluminium-works at Nanterre near Paris, and later on at Salyndres (in 1861 and 1862), by mixing it with common salt and passing steam into the mixture in a closed vessel, or, better, in a reverberatory furnace at a high tem-

perature. In what way the volatilization of the salt was prevented and the HCl condensed has not become known; but it is a fact that the aluminate sent into the trade by Morin was not made from common salt but from sulphate. On July 12, 1862, Gossage again patented a process, similar to Tilghman's, but employing a peculiar furnace, which we shall describe when mentioning the silica process, proposed at the same time and preferred by himself. On the 18th July, 1874, Grüneberg and Vorster took out an English patent upon the same subject. Common salt and alumina are made into a paste; the mass is dried, broken into small pieces, and treated with red-hot steam. HCl escapes, and $Na_2Al_2O_4$ remains behind. The latter is dissolved out from the impurities, and decomposed either by CO_2 or by CaO, according to whether carbonate or caustic soda are to be obtained. In lieu of alumina, ferric oxide or any other metallic oxide may be employed (?). This process was actually tried, but had to be discontinued because the vessels would not stand—the same drawback which has opposed itself to so many theoretically sound processes. A recent German patent by Lieber (No. 9610, Nov. 10, 1878), proposes mixing alkaline chlorides with magnesium sulphate (occurring at Stassfurt as kieserite) and as much crude alumina (in the state of bauxite &c.) as will decompose the alkaline sulphates formed. The mixture is moulded into bricks, which are dried and heated to a red heat in a kiln, steam being passed through at the same time. First there are formed alkaline sulphates and hydrochloric acid. The latter is condensed in the usual manner; the sulphates are acted upon by the alumina, sulphur dioxide and alkaline aluminate being formed. The ignited mass is lixiviated with water, and treated with carbon dioxide, so that alkaline carbonate and a precipitate of aluminium hydroxide are obtained. In lieu of HCl, chlorine may be obtained by submitting the dried mass at 900° to a gentle current of air, previous to igniting it in the kiln.

13. *By means of aluminium chloride.*—Swager (Monit. Scientif. 1868, p. 838) proposes to mix a solution of NaCl and of Al_2Cl_6; the double salt, 2NaCl, Al_2Cl_6, is obtained by drying, and blown by means of a fan-blast, in the form of a fine powder, through a red-hot retort in which it is exposed to superheated steam. Sodium aluminate and HCl are generated; the former is decomposed by CO_2 into Na_2O_3 and Al_2O_3, which is again converted into Al_2Cl_6.

14. *By means of silica and steam.*—On melting, silica and com-

mon salt do not unite, but the latter melts much sooner than the former, lies as a cover on the silica, and evaporates before the latter can come into action. Only in minimal quantities and quite superficially does combination take place—for instance, in the salt-glazing of earthenware; but here the salt acts in the state of vapour, and the reaction is probably only made possible by the aqueous vapour existing in the fire-gases. In order to utilize this reaction on a large scale, steam must be applied to begin with. Already, in 1809, Gay-Lussac and Thénard founded upon this a proposal for soda-making. Blanc and Bazille on February 12, 1840, obtained an English patent for this process, which they intended to carry out in this way:—280 parts of common salt and 200 of sand, intimately mixed, are loosely put into horizontal cast-iron cylinders, entirely surrounded by the flame, and heated to a cherry-red. Through the axis of each cylinder passes a wide tube, perforated with many holes, for introducing steam; at the end of this tube a wide porcelain or stoneware pipe carries off the vapour of NaCl and HCl. The steam must enter equably and slowly, so that the temperature shall never sink below a cherry-red heat; in that case the decomposition of the mixture into neutral sodium silicate and hydrochloric acid (according to the formula

$$2NaCl + SiO_2 + H_2O = Na_2SiO_3 + 2HCl)$$

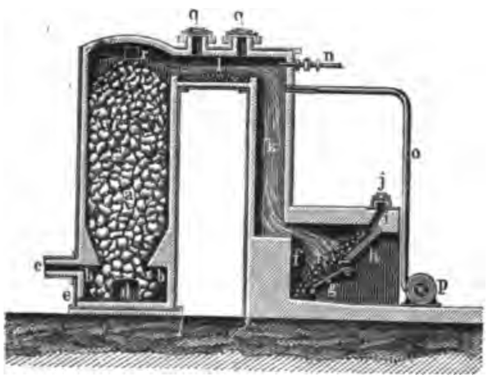
becomes easy and complete [?]. The exit-tube for the gases ends in a wide chamber for depositing the volatilized salt, which is then continued into an apparatus for condensing HCl; this, however, must work at a very low pressure. The neutral sodium silicate obtained as above is very slightly soluble; consequently it can be deprived of undecomposed common salt by crushing and washing, and by melting with two thirds of its weight of soda is converted into soluble basic water glass. The latter is drawn out hot into cold water, dissolved, and, by a current of CO_2 from a lime-kiln, decomposed into sodium carbonate and gelatinous silica. The latter can be employed for the manufacture of fine glass. It is evident that this process is useless: for each 100 parts of crude silicate 60 parts of soda-ash are sacrificed; and afterwards, on washing the gelatinous silica, undoubtedly much soda is again lost, —all this independently of the difficulties in decomposing the salt.

Fritsche in 1858 obtained an Austrian patent for converting

common salt into soda by means of silica and steam; no particulars are stated (Wagner's Jahresb. 1858, p. 118).

In England the same process has been the subject of several patents; the only one, however, which in the beginning promised to become successful was that of Gossage (July 18, 1862). He employed a peculiar apparatus, sketched in fig. 161: *a* is a tower

Fig. 161.



made of fire-bricks, tapering near the bottom and then widened out again; it is nearly filled with pieces of quartz or flints; at the bottom at *b* a space remains free, which communicates with the flue *c* for taking away the gases. More quartz can be thrown in through the opening *d*, which is usually closed. The melted sodium silicate can flow away through the opening *e*. In the gas-generator *f* coals are burnt with insufficient access of air, so that combustible gases are formed; *g*, grate-bars; *h*, slanting fire-plate; *i*, charging-hopper; *k l*, gas-flue; *n*, pipe for introducing steam; *o*, pipe for introducing air compressed by the fan-blast *p*. The bottom of the flue *l* is charged with salt through the openings *q q*. Through *r* more quartz can be put in. By means of the generator *f* and the fan-blast *p* a very great heat can be produced in the tower *a*; when this has been attained, salt is put in through *q q*, which volatilizes and, by the assistance of steam from *n*, decomposes the hot quartz; sodium silicate is formed, together with hydrochloric acid, which escapes from *c* with the residual gases and is condensed (not very readily!). The sodium silicate is employed for glass-making or as water glass; or it is decomposed by means

of CaO into NaOH, or by introducing CO_2 into Na_2CO_3. The same apparatus may be charged with alumina in lieu of quartz, and sodium aluminate obtained (see above)—or with clay, or clay-slate, or felspar, granite, &c., in which cases mixtures of sodium silicate and aluminate are obtained.

The latter Gossage probably never realized; but he certainly made sodium silicate for some time in the manner described, and exhibited soda obtained from it in Paris in 1867. At what cost it was obtained was not stated; so much is certain, that the process had to be given up entirely: the apparatus could not resist the enormous heat; the decomposition was very incomplete, and the HCl difficult to condense.

Brisse endeavoured to improve Gossage's process by heating salt to the melting-point on the sloping bottom of a reverberatory furnace, adding silica in the state of fine powder, and conducting superheated steam through the mass. "The sodium silicate thus obtained is treated with calcium carbonate at a high temperature and the mass lixiviated, whereby sodium carbonate and calcium silicate are obtained, from which silica is separated by hydrochloric acid" (sic!) "and used over again."

Whilst the processes just described are evidently useless, a proposal made by Ungerer (Dingl. Journ. cxcvii. p. 343) does not seem entirely impracticable. He proposes to get the mixture of salt and sand, by means of steam and heat, up to the fritting-point, and then to employ it for glass-making; he does not even mention any possible use of the frit for soda-making, which no doubt its slight solubility would prevent.

As a curiosity it may be mentioned that, on February 24, 1854, Cowper (for Laureau) patented the decomposition of natural or artificial silicates by six months' "*fermentation*" with alternate layers of straw, sawdust, &c. After that time the mass was to be impregnated with thick milk of lime and calcined in a furnace; on lixiviation it was to yield very pure soda; and the residue was to be employed as pozzuolana!

15. *By means of chromium oxide and steam.*—C. Kessler, in 1867, patented in France the following process:—Sodium (or potassium) chloride is intimately mixed with chromium sesquioxide, alone or along with manganese, or with chrome iron-ore or lead chromate, and in a red-hot state treated with superheated

steam. With the assistance of atmospheric oxygen, sodium bichromate and hydrochloric acid are formed—

$$2NaCl + Cr_2O_3 + H_2O + 3O = Na_2Cr_2O_7 + 2HCl.$$

When the reaction is finished and the mass cooled down, it is mixed with coal and again heated to a dark-red heat. Now sodium carbonate and chromium oxide are formed, CO or CO_2 being given off—

$$Na_2Cr_2O_7 + 2C = Na_2CO_3 + Cr_2O_3 + CO$$

or

$$2Na_2Cr_2O_7 + 3C = 2Na_2CO_3 + 2Cr_2O_3 + CO_2.$$

The sodium carbonate is dissolved out, and the residual Cr_2O_3 used for decomposing fresh salt. This proposal is impracticable, because the reaction between Cr_2O_3, NaCl, and superheated steam (already patented by Swindells in 1851) is very incomplete.

Rather different is the patent of Hargreaves and Robinson, dated February 17th, 1872. The alkaline chromates, obtained in the chlorine process patented by the same inventors, are to be reduced by hydrogen, carbonic oxide, or hydrocarbons; in the first case the hydrates, in the latter cases the carbonates of the alkalies are obtained. Or the chromates are reduced by heating with finely divided coal (as in Kessler's), and cooled in closed vessels, to prevent the re-formation of chromates.

16. *By means of carbonic acid.*—Although no one has actually proposed the employment of carbonic acid for soda-making, it should be mentioned that Hugo Müller (Deutsch. chem. Ges. Ber. ii. p. 40) has noticed that CO_2 is somewhat more soluble in water containing NaCl than in pure water, a little NaCl being decomposed by CO_2, and HCl being liberated; the latter can be proved by the destructive action of the HCl upon ultramarine. It is wonderful that nobody has yet taken out a patent for alkali-making on the strength of this reaction!

17. *By means of boric acid.*—Böhme found, in 1848 (Wagner's 'Regesten,' p. 23), that boric hydrate decomposes common salt, in the presence of steam, into sodium borate and hydrochloric acid. The former might be converted by lime into caustic soda and calcium borate, and from the latter the boric acid regenerated (no doubt by HCl!), to be used again. This proposal, which the high

price and inevitable loss of boric acid makes appear chimerical, was patented by Margueritte on Jan. 20th, 1855.

18. *By means of ammonium carbonate.*—To this process Chapter XVI. will be entirely devoted.

19. *By means of calcium sulphide.*—According to Greenshield's patent (Dec. 22nd, 1853), gypsum and small coal are to be brought to a red heat and common salt and more small coal added, and heat applied till no more gas is given off; the mass is cooled and lixiviated, the solution boiled down; and the salt obtained is fused in a black-ash furnace with coal and chalk. The description of the process is very obscure, but does not invite any special study.

20. *By means of steam only.*—Sheridan, on Aug. 31st, 1837, patented the decomposition of common salt in the state of vapour by steam "or hydrogen" at a bright-red heat. He figures an apparatus consisting of two conical furnaces; the inner one serves for receiving the salt and introducing the steam, the outer one for forming and removing the alkali and the vapour of HCl.

Swinburne, on Nov. 21st, 1862, patented the same thing; and so did Gillard on July 16th, 1861, and July 22nd, 1865 (steam of 1000° C. was to be employed, and introduced into the melted salt through platinum tubes).

Powers and Dale (patent of Jan. 10th, 1863) propose the same, but hope to assist the decomposition by adding oxide of iron, aluminium, or manganese.

Henry (for Laurent) obtained provisional protection, Dec. 26th, 1865, for decomposing melted sodium chloride by superheated steam.

Weldon, on Oct. 26th, 1866, patented the same, along with the decomposition of sodium fluoride or nitrate by steam, indicating special heating-appliances.

Cabot (Chem. News, xxxi. p. 243) describes laboratory experiments on decomposing common salt by superheated steam; he obtained hydrochloric acid and alkaline ashes. Evidently the reaction $2\,NaCl + H_2O = Na_2O + 2\,HCl$ had taken place; but "of course the yield was no approach to the theoretical one, and it could not be applied as a technical process."

Similar experiments were made by Viedt (Wagner's Jahresb. 1875, p. 383) without any practical result; but he did not abandon all hope of final success.

21. *By means of the galvanic current.*—Cook's patent of May 3rd, 1851, prescribes that a tank is to be divided by two porous diaphragms into three compartments, copper plates placed in the middle, and large pieces of iron in each of the other two, and connected with the copper plates by slips of copper; the middle compartment is filled with water, the two outer ones with a solution of common salt. If the temperature is kept above 21° C., the decomposition of the salt is said to be accomplished within seven days. Soon after (on Sept. 25th, 1851), C. Watt describes the same process much more explicitly and extended to many salts; and the same thing was patented by Stanley on April 5th, 1853. Such processes could in any case only become useful if the electricity required for decomposing a molecule of common salt could be generated with the expenditure of less coal than we require in the ordinary process, which undoubtedly is not the case.

II. Soda from Sulphate.

A. *Without converting it into Sulphide.*

1. *By means of lime.*—Already in 1789 Delius intended decomposing sulphate by lime into caustic soda and gypsum; afterwards Achard, Scheele, Klaproth, Göttling, and Westrumb occupied themselves with the same matter, and, indeed, made soda by this process. Anthon in 1840 showed that the decomposition is only imperfect (Wagner's 'Regesten,' p. 46). Claussen, on Feb. 3rd, 1852, took out an English patent for manufacturing sodium hydrate and carbonate by boiling sodium sulphate with the hydrate of calcium, barium, or strontium: the earthy sulphate is precipitated; and NaOH remains in solution; by long exposure to the air it is changed into carbonate. Common salt is also decomposed "by means of certain organic acids, which are afterwards decomposed by heat," by "gaseous acids," by "hydrates, oxides, peroxides, and certain metallic bases; also by certain carbonates, carbonate of ammonia excepted." From this medley every body may pick out what suits him. A better result than by boiling with quicklime under ordinary circumstances was expected to be attained by Hunter (patent dated April 8th, 1865) by boiling under pressure. Good results were to be obtained with sulphate of soda "by boiling a solution of sp. gr. 1·100, at a pressure of from 40 to 50 lb. per square inch," and with sulphate of potash "by boiling a solution of

sp. gr. 1·100, at a pressure of from 80 to 90 lb. per square inch, till a test shows that the reaction is finished. An excess of lime is useful, and may be utilized by employing the residue of $Ca(OH)_2$ and $CaSO_4$ for the first treatment of a fresh portion of alkaline sulphates, and decomposing the latter by a second boiling with fresh quicklime. Some varieties of lime are less active than others. The gypsum is separated from the caustic lye by filtering under pressure, lest any backward decomposition set in; and the caustic soda is used as such or converted into carbonate by introducing CO_2 or by evaporating over $CaCO_3$." Hill (Chem. News, xxvii. p. 165) examined the action of lime on sulphate with or without pressure, and obtained very discouraging results. By boiling without pressure he could only obtain 1 per cent. of the sulphate as NaOH; at a pressure of nearly 3 atmospheres only 6 per cent., and at a pressure of 13 atmospheres, continued for several hours, only 13 per cent. was converted into NaOH.

2. *By means of caustic baryta.*—Undoubtedly the decomposition of sodium sulphate and barium hydrate to barium sulphate and sodium hydrate, which takes place even in cold solutions directly and completely, would be an extremely convenient soda-making process, *if* the preparation of caustic baryta were possible in a simple and cheap way; but the prospect of realizing this indispensable condition is as far distant as ever.

Patents for this process have been granted:—to Fuller (April 3rd, 1819), who intended making caustic baryta by heating carbonate, and utilizing the CO_2 driven off for carbonating the caustic soda; further, to Samuel (Nov. 13th, 1838), who employed the sulphides of barium and strontium, made from the sulphates by reduction with coal, and converted the sodium sulphide formed into carbonate by means of CO_2; moreover he patented the direct application of barium or strontium hydrate, made from the sulphides by means of copper oxide. Anthon in 1840 tried Samuel's process, and obtained good results.

R. Wagner (Regesten, p. 50) also found that sodium sulphate is easily and completely decomposed by caustic baryta at all temperatures and pressures, and that, as H. Rose had stated, a solution of sodium hydrate, if CO_2 is kept off, does not act upon $BaSO_4$. Hofacker (Dingl. Journ. clxix. p. 76) made again the "novel" proposal of employing caustic baryta, obtained by calcining the native carbonate or by reducing the sulphate and treating the BaS

with CuO, for decomposing sodium sulphate; and Hunter, on Nov. 17th, 1864, patented the same thing.

All these proposals must remain futile until a *much* cheaper process for making caustic baryta than any of those known hitherto has been discovered. *When* this is done, then certainly, as Hofmann says (Report by the Juries, 1863, p. 64), the alkali-manufacture will be revolutionized; but depending upon such "whens" any revolution whatever may be made. Hofmann adds very justly that in such a case the use of caustic baryta would mostly supersede that of caustic alkaline lyes.

3. *By means of caustic strontia* (comp. also nos. 1 and 2).—Ungerer (Dingl. Journ. clxxxviii. p. 140) makes the following proposal. First, by boiling equivalent quantities of ammonium sulphate and sodium chloride in concentrated solutions, anhydrous sodium sulphate is to be obtained, which is precipitated and fished out; on cooling, ammonium chloride crystallizes; and the mother liquor on evaporation again furnishes sodium sulphate. The latter, dissolved in water and mixed with caustic strontia, yields very pure caustic soda and a precipitate of strontium sulphate. The ammonium chloride previously obtained is converted by calcium carbonate into ammonium carbonate; and this, digested with the strontium sulphate, yields strontium carbonate and ammonium sulphate. The latter serves for decomposing fresh salt; the former is mixed with coal and ignited in a reverberatory furnace with the assistance of steam, till it has given up its carbonic acid, which is easily done. Thus the raw materials are only common salt and lime and as much strontia [and ammonia !] as is required for replacing the inevitable loss in manufacturing. The hydrochloric acid is certainly lost with the calcium chloride. Ungerer points out as advantages of his process that strontium sulphate can be converted into carbonate by digestion with ammonium carbonate, and that strontium carbonate more easily yields up its CO_2 than $BaCO_3$. But he himself admits that the decomposition of $SrSO_4$ is not perfect; strontium sulphide is formed, and consequently sodium sulphide, and that in considerable quantity. Even apart from that, this ingeniously combined process is useless; a considerable quantity of $SrCO_3$ will not be changed into SrO, and will consequently be lost; and the loss of ammonia will be even worse. If ammonia is to be employed at all, no doubt the much simpler process of Dyar and Hemming will be resorted to.

4. *By means of calcium bicarbonate.*—Pongowski (French patent of March 27th, 1872) adds to a solution of alkaline sulphate a little more than the theoretical quantity of finely powdered limestone, covers up the vessel, and conducts a current of CO_2 into it, constantly agitating. Calcium bicarbonate is formed, which is decomposed with the alkaline sulphate; after eight hours the latter is completely converted into carbonate. The mixture is allowed to settle, the liquid poured off from the precipitate and boiled down.

5. *By means of strontium carbonate.*—Most of the proposals made for barium carbonate also refer to this.

6. *By means of barium carbonate.*—According to Wagner's 'Regesten,' p. 46, the first experiments with this were made in 1826 by Kastner at Erlangen, and that in the dry way, but unsuccessfully; Anthon, on repeating, in 1840, Kastner's experiments, was no more fortunate. Kölreuter first tried the wet way, in 1828. He prescribed the precipitation of barium carbonate from a solution of chloride by means of ammonium carbonate, washing out the precipitate, putting it in the state of paste into a solution of sodium sulphate, and boiling for an hour with the latter. One part of $BaCO_3$ (calculated as dry) is to decompose two parts of crystallized sodium sulphate, and to yield 1½ part of soda crystals. But it is a fact that in this way, even with an excess of $BaCO_3$ and on boiling, Na_2SO_4 can never be completely decomposed. This was confirmed in 1832 by Erdmann and Buchner. C. Lennig in 1851 received a patent in several German States for a process of making soda from sulphate by means of barium carbonate. In England an anonymous person obtained a patent, through H. Taylor, on March 15th, 1851. This patent refers to barium and strontium salts, and prescribes the regeneration of their carbonates from the sulphates by reduction to sulphides and application of CO_2; the H_2S escaping is to be burnt into S and H_2O, or into SO_2 for acid-chambers. He also mentions that the decomposition of the sulphates with barium or strontium carbonate is "facilitated" by a current of CO_2; but he was evidently not acquainted with the *necessity* of this addition, nor does he give any special instructions for carrying out the above-mentioned reactions, which are merely mentioned as suggestions. On April 23rd, 1856, Balmain and Colby again patented the reaction between $BaCO_3$ and the alkaline sulphates, without any essential innovation. In 1858 Kessler again drew attention to barium

carbonate; also Hofacker, who started from the erroneous supposition that $BaCO_3$ and Na_2SO_4 are smoothly and easily converted into Na_2CO_3 and $BaSO_4$. But unfortunately a large portion of Na_2SO_4 always remains undecomposed, at whatever temperature the operation may be conducted. Hill (Chem. News, xxvii. p. 165) mentions that on boiling equivalent quantities of sodium sulphate, barium carbonate, and lime under pressure (but what pressure?) a complete conversion into caustic soda had been attained, but himself doubts the possibility of recovering the barium carbonate from the mixture of barium sulphate and calcium carbonate in an economical way.

Much better results are obtained by working with barium bicarbonate; in this case complete decomposition can be obtained with equivalent quantities of the two salts. In 1857 R. Wagner (Jahresb. 1857, p. 104) proved that a clear solution of barium bicarbonate, obtained by passing CO_2 (no doubt in great excess) through $BaCO_3$ suspended in water, decomposes with Na_2SO_4 into $BaSO_4$ and $NaHCO_3$; but this process, considering the very slight solubility of barium bicarbonate (1 : 800 water), cannot lay claim to any technical value.

A further step was taken by Kuhlmann (Hofmann, Report by the Juries, 1863, p. 32), who, on repeating Wagner's experiments, got better results by employing a pressure of three or four atmospheres, simply because then a somewhat more concentrated solution of barium bicarbonate can be obtained. Very important was the remark made by Wagner in his 'Jahresbericht,' 1864, p. 166, that complete conversion of $BaCO_3$ into $BaH_2(CO_3)_2$ is not necessary, and that a comparatively slight proportion of the latter may make the decomposition of Na_2SO_4 perfect. For all that, the great dilution of the liquids prevented an industrial application of the process; and this was only approached by a proposal made by Brunner (Dingl. Journ. clxxvi. p. 127). It consisted in dissolving 1 part of sodium sulphate in 30 or 40 parts of water, suspending in it 2 parts of barium carbonate obtained by precipitation, and passing through the liquid at the ordinary temperature a current of carbonic acid, with frequent shaking or stirring. With a few grams of substance the decomposition was complete in an hour. The resulting solution contains, besides sodium bicarbonate, a little barium bicarbonate, which on boiling is decomposed into CO_2 and precipitated $BaCO_3$. Of natural barium carbonate, finely ground, a large

excess (about four times the quantity of sodium sulphate) is required. In order to prepare precipitated $BaCO_3$, which is more active, native sulphate of baryta was to be ignited with powdered coal and rosin in a crucible, the product lixiviated with water, and the solution treated with CO_2. Any barium sulphide remaining in the precipitate does no harm, as it is not decomposed afterwards. The carbonic acid for this process was to be prepared by means of limestone and hydrochloric acid (sic !); "but since the quantity of HCl obtained in decomposing the NaCl is not sufficient for supplying the quantity of CO_2 required for this process, some more must be made in different ways, of which a sufficient number are known" (!). This proposal is proved, in each sentence, to have proceeded from a purely laboratory point of view, with complete ignorance of the conditions required in practice. What should be done with the sulphuretted hydrogen is not even hinted at by Brunner.

The author of this treatise, unacquainted with either Taylor's patent or Brunner's proposal (the latter of which was only published after he had completed his own labour), but incited by Wagner's publications, independently hit upon the plan of making the process technically possible by not commencing with a solution of barium bicarbonate, but passing carbonic acid into a solution of sodium sulphate in which barium carbonate was suspended; the small quantity of barium bicarbonate formed would at once decompose sodium sulphate, and would be removed from the liquid as barium sulphate, thus enabling the liquid to dissolve a further quantity of barium bicarbonate, and so forth, till all the sodium sulphate was decomposed. But in order not to lose too much carbonic acid and to make the regeneration of barium carbonate feasible in an economical way, a combination of apparatus and processes was thought out, which is described in an English patent of April 20th, 1866, and in the 'Chemical News,' xxvii. p. 139. Here we shall only mention the principal features very briefly. The CO_2 is made by burning coke, or taken from a lime-kiln, or purified by Ozouf's plan (that is, first passing it through a solution of sodium carbonate, which allows the indifferent gases to escape, and on boiling gives off pure CO_2). It then passes through several closed iron cylinders, provided with mechanical agitators, containing a solution of sodium sulphate along with a sufficient quantity of precipitated barium carbonate; when the decomposition is finished in the first cylinder, the gas is turned on to the

second cylinder, whose contents are partially finished, whilst the first cylinder is getting emptied and refilled, and then receives the gas issuing from the other cylinder. As, however, the current of CO_2 must be a strong one and a good deal of it escapes even from the second cylinder, the gas is conducted through further vessels, in which it acts upon barium sulphide, and thus the CO_2 is completely spent; H_2S escapes, mixed with indifferent gases; and $BaCO_3$ is precipitated. The latter is at once utilized in the state of mud in the first cylinder. The barium sulphide is obtained from the $BaSO_4$ formed in the first vessels, by igniting with coal and lixiviating, which with proper apparatus presents no difficulty. Up to this stage the author had actually carried out the process on a pretty large scale. For the most difficult part of his task, the utilization of the H_2S, he had in his patent made several proposals, which, however, were never practically tried, and which undoubtedly could not have been carried out exactly in the way proposed on any really large scale. In his publication the author himself admits that his process would cost more for plant and working expenses than Leblanc's; but a much larger yield and much purer carbonate is obtained by it; and he thought it well adapted for making such pure alkali, provided that the difficulty of disposing of the sulphuretted hydrogen could be satisfactorily overcome. Now-a-days the author would not consider his own proposal able to compete, even for pure alkali, with the ammonia process, which likewise supplies very pure soda.

Three years later Puissant patented something similar in France. He is silent on the recovery of $BaCO_3$; and he proposes decomposing the solution of sodium bicarbonate with lead sulphate into sodium sulphate and lead carbonate, the latter to serve as white lead [which it cannot do]. This is properly only a white-lead process, and that an impracticable one. Lawrence Smith in 1873 ('Chemical News,' xxvii. p. 310) described the same process (with barium carbonate, carbonic acid, and sodium sulphate) as one never before described (!); he adds the proposal to prepare the alkaline carbonates by calcining the tartrates or oxalates, which can be obtained from barium carbonate, sodium sulphate, and the organic acid. Of course this could not be intended for a technical process at all.

7. *By means of calcium acetate.*—Proposed by Crell in 1778, by Millet in 1822, by Mollerat and Payen, and by Lampadius.

8. *By means of lead acetate* (Kirwan, in 1789).

9. *By means of barium acetate* (proposed as late as 1842 by Anthon).

These three proposals possess only historical interest; equally so the following, namely

10. *By means of potassium carbonate* (Wagner's 'Regesten,' p. 45).—C. F. Hagen showed, in 1768, that from a mixed solution of sodium sulphate and potassium carbonate first a crop of potassium sulphate, and then one of sodium carbonate is obtained. Bergman (1781), Wiegleb, Göttling, Accum, Nasse have each described this process, which, at the then ruling prices of potash and soda, was not so completely absurd in an economical point of view as in 1840, when Anthon thought it worth while to try it on a large scale and pronounce favourably upon it!

11. *By means of ammonium carbonates.*—According to Bower's patent of March 4th, 1840, in a cylinder provided with mechanical agitating-gear 86 parts of ordinary ammonium (sesqui-) carbonate are stirred for 18 to 24 hours with 100 parts of sodium sulphate and 200 water, and a current of carbonic acid is passed through the mixture; there result a precipitate of sodium bicarbonate and a solution of ammonium sulphate. The ammonium sulphate can serve for decomposing common salt; and from the ammonium chloride the bicarbonate is regenerated. The sodium bicarbonate is converted into monocarbonate by ignition in a closed vessel; so that the adhering ammonium salt is not lost. The process of Gerlach, to be described in the 16th Chapter, is essentially the same as the above. It cannot very well compete with Dyar and Hemming's ammonia process.

12. *By means of alumina as bauxite and of ferric oxide respectively.*—Sodium sulphate mixed with alumina is not decomposed even at a white heat, but is decomposed if steam is admitted. In Tilghman's patent of 1847 (see p. 317) this process was also described. Wagner (Jahresb. 1865, p. 328) found that on working in a muffle (that is, excluding the CO_2, which acts upon the aluminate), even with three equivalents of Al_2O_3 to one of Na_2SO_4, at most only 40 per cent. of the sulphate could be converted into aluminate, the muffle being very strongly corroded. Bauxite behaves similarly; ferric oxide acts better, but only at an extremely high temperature, hardly attainable in manufacturing-practice. The soda of the sulphate is easily convertible into aluminate if coal is added to the mixture and then heat applied; but bauxite, which

always contains iron, cannot be used in this way, because with it the well-known ferro-sodic sulphide is constantly formed. The recommendation of the process by Balard (Höfmann, Report by the Juries, 1863, p. 69) takes no account of this.

Bauxite is a connecting link between diaspore (pure $Al_2(OH)_6$) and brown hematite; the more the iron predominates in it, the more the white colour passes into brown. It was originally found in France near the village of Baux; in the departments of Var and of the Bouches du Rhône, from Tarascon to Antibes, a distance of 100 miles, many deposits are found, some of them several dozens of yards thick. Deposits are also found in the departments de l'Hérault and de l'Ariége. Quite recently very good bauxite has been found at Hadamar in Hessia. Very important deposits were found by Fleckner in the Austrian province of Krain, on the Sava in Wochein, and on the Feistritz. This mineral, also called wocheinite, is of dense earthy structure, whilst the varieties occurring in France, and also in Ireland (at Irish Hill and Straid, co. Antrim), are oolitic conglomerates. The following analyses (p. 334) give an idea of the varying proportions of alumina and ferric oxide; besides the constituents mentioned here, the bauxites contain traces of lime, magnesia, sulphuric, phosphoric, titanic, and vanadic acids. The Irish-Hill bauxite is stated to be almost free from iron.

Instead of decomposing the sodium aluminate by CO_2, in which case a modification of alumina not easily soluble in acetic acid is formed, Löwig Brothers (German patent no. 93, 1877) add milk of lime to an aqueous solution of sodium aluminate, whilst heating it, till the liquid has become completely caustic and all the alumina is precipitated; then caustic alkali remains in solution, and a perfectly insoluble compound of Al_2O_3 with 3CaO is precipitated. The latter is separated from the caustic lye, divided into two halves, one half completely dissolved in hydrochloric acid, while the other half, made into a cream with water, is added until a filtered sample shows slight traces of alumina in solution. Calcium chloride passes into solution; and a modification of aluminium hydrate remains behind, which is adapted in an eminent degree for decolorizings, especially of sugar-liquors, and is also readily soluble in acetic acid. An additional patent, No. 1650 (Dec. 21, 1877), describes the preparation of sodium aluminate from bauxite or (more correctly) cryolite; but as it starts from fusion with sodium carbonate, and

Analyses of Bauxite.

(Partly from Biedermann, in Hofmann's Bericht, i. p. 619.)

	a.	*b.*	*c.*	*d.*	*e.*	*f.*	*g.*	*h.*	*i.*	*k.*	*l.*
Alumina	60	75	63·16	72·87	44·4	54·1	64·6	45·77	55·61	56·0	76·3
Ferric oxide	25	12	23·55	13·49	30·3	10·4	2·0	18·97	7·17	6·2	8·4
Silica	3	1	4·15	4·25	15·0	12·0	7·5	6·41	4·42	11·0	14·9
Na_2O and K_2O	...	...	0·79	0·78	...	...	...	0·38	...	...	...
Water	12	12	8·34	8·50	9·7	21·9	24·7	27·61	32·33	26·4	...
Calcium carbonate	...	...	...	...	...	...	...	0·55	0·39	...	...

a and *b* from Baux (Ste.-Claire Deville); *c*, dark wocheinite; *d*, light ditto (Drechsler); *e*, reddish brown, *f*, yellow, *g*, white bauxite from Feistritz (Schnitzer); *h* and *i*, Hadamar bauxite (Dingler's Journ. ccxxix. p. 274); *k*, bauxite from Klein-Steinheim (Baden), analyzed by Bischof; *l*, the same, calcined.

its proper object is the preparation of pure alumina along with caustic soda, we must refer to the patent itself. The reactions employed in Löwig's process are :—

I. $Na_6Al_2O_6 + 3Ca(OH)_2 = 6NaOH + Ca_3Al_2O_6$.

II. $Ca_3Al_2O_6 + 12HCl = 3CaCl_2 + Al_2Cl_6 + 6H_2O$.

III. $Ca_3Al_2O_6 + Al_2Cl_6 + 6H_2O = 3CaCl_2 + 2Al_2(OH)_6$.

13. *By means of silica.*—Water glass (sodium silicate) was long since made by melting together sand, sodium sulphate, and coal, SO_2 escaping; but as the material of the furnaces was quickly destroyed, most manufacturers prefer making water glass by fluxing sand with sodium carbonate. From the water glass, by introducing CO_2, an aqueous solution of sodium carbonate can be obtained, but much more expensively than by Leblanc's process; for the furnace-process is not done away with, and carbonic acid is not to be had for nothing. The proposal to employ the separated silica over again for decomposing sulphate does not mend matters, since ordinary sand will do as well. From the solution of water glass also caustic soda, along with calcium silicate, can be obtained by boiling with lime. One of the greatest difficulties in this process is the washing of the gelatinous hydrate of silica. The separation of the calcium silicate from the caustic lye is said to be less difficult: but here also great difficulties must exist; for this seemingly advantageous plan for making caustic soda is not employed, although it has been known for generations. In February 1874 the St.-Gobain Company took out a French patent for this old process. It prescribes melting 71 parts of sodium sulphate, 80 parts of Fontainebleau sand, and 8 or 9 parts of small coal in a closed crucible, dissolving, and making from the solution either sodium carbonate by means of CO_2, or caustic soda by means of lime. The SO_2 escaping during the melting is to be used in sulphuric-acid making (but *how*, in the presence of carbonio acid?). It is almost needless to say that this process has not been carried out to any great extent.

14. *By means of galena or blende* (Wagner's 'Regesten,' p. 53).—Baudrimont and Pelouze noticed (1833) that, on heating sodium sulphate with galena in the presence of silica, sodium plumbate (Na_2PbO_2) was formed. How this reaction is to be practically carried out is not stated in our authority; but the addition is made that blende may be substituted for galena.

15. *By means of hydrofluoric acid.*—Among the three soda-

making processes which Weldon patented on March 1st, 1866, there is one employing hydrofluoric acid, which comprises the following stages :—" 1st. Sodium chloride and magnesium sulphate are mutually decomposed, either in the dry way or, better, by mixing their solutions and cooling down to -4° C.; sodium sulphate crystallizes out; and the mother liquor, by boiling down the $MgCl_2$ and heating, is decomposed into MgO and HCl [incompletely !]. 2nd. The Na_2SO_4 is treated with aqueous solution of HFl, which causes the formation of hydrosodic sulphate and sodium fluoride

$$(Na_2SO_4 + HFl = NaHSO_4 + NaFl).$$

The treatment takes place in the cold in a suitable vessel lined with lead or gutta percha &c., and is finished by a few minutes' stirring; NaFl settles down as a dense precipitate; $NaHSO_4$ remains in solution. 3rd. This NaFl is decomposed by the magnesia obtained in 1, by boiling in an aqueous solution, caustic soda and magnesium fluoride being thus formed,

$$2\,NaFl + MgO + H_2O = 2\,NaOH + MgFl_2.$$

4th. The $MgFl_2$ from the 3rd operation is decomposed by the $NaHSO_4$ from the 2nd into magnesium sulphate, hydrofluoric acid, and sodium fluoride:

$$2\,MgFl_2 + 2\,NaHSO_4 = 2\,MgSO_4 + 2\,NaFl + 2\,HFl."$$

This also is said to take place at a slightly elevated temperature; and "thus all the materials, except salt and coal, are recovered" [in theory].

The following is mentioned as a still shorter method :—1st. Sodium fluoride is decomposed by superheated steam into caustic soda and hydrofluoric acid,

$$NaFl + H_2O = NaOH + HFl.$$

2nd. As in the 2nd stage of the preceding, sodium sulphate is decomposed with the HFl from No. 1 into hydrosodic sulphate and sodium fluoride, the latter serving again for the 1st operation. 3rd. The hydrosodic sulphate is by common salt decomposed into sodium sulphate and hydrochloric acid, and the former employed for the 2nd operation:

$$NaCl + NaHSO_4 = Na_2SO_4 + HCl.$$

Neither of these plans has found, or is likely to find, any practical application.

According to Jean (Comp. Rend. lxvi. p. 801), by melting 100 parts of fluorspar with 140 of calcium carbonate, 200 sodium sulphate, and coal in excess a mass can be obtained which on lixiviation yields a clear solution of NaFl, free from Na_2S, according to the equation

$$2\,CaFl_2 + 2\,Na_2SO_4 + 2\,CaCO_3 + 13\,C = 4\,NaFl + CaO + 2\,CaS + 13\,CO.$$

[This equation is wrong; but we might put it

$$2\,CaFl_2 + 2\,Na_2SO_4 + CaCO_3 + 9\,C = 4\,NaFl + CaO + 2\,CaS + 10\,CO.]$$

The sodium fluoride is easily obtained in the pure state by evaporation and crystallization. Experiments made in the author's laboratory showed that but little sodium fluoride is formed, and that it can be obtained in a pure state only in the first lixiviation; the next washings constantly contain more sodium sulphide, generated by the reaction of the sodium carbonate, formed at the same time, upon calcium sulphide in the presence of air.

16. *By means of aluminium phosphate.*—G. E. Davis has quite recently (Kingzett, 'Alkali-trade,' 1877, p. 165; Journ. Soc. of Arts, 1877, p. 633) patented the following process:—"Rodondo phosphate (commercial, consisting principally of aluminium phosphate) is mixed with sand, sodium sulphate, and small coal, all in the state of powder, and the mass heated in an ordinary black-ash furnace, but not up to the fluxing-point, which, indeed, would not be possible within a reasonable time. When the decomposition is complete, the charge is drawn into an iron bogie, and even without cooling is ready for lixiviation. The best sand to use for this process is that which comes from the grinding and polishing of plate glass, which, being a waste product, costs the glass-works a large sum of money to remove. During the process sulphurous acid, arising from the decomposition of sulphate, escapes from the furnace and may be utilized for the production of sulphate by Hargreaves's process, or of sulphites, provided the heating takes place in a close roaster; if the gas be not required, an ordinary furnace or revolver may be employed" [this is a very weak point of the process; the escape of all the SO_2 into the air could never be tolerated; and if close roasters

are employed, the expense will be too large]. Several charges worked on the large scale in an ordinary hand black-ash furnace were compounded as follows—aluminium phosphate 1·5 cwt., sulphate 2·75 cwt., waste sand 0·75 cwt., small coal 0·75 cwt. Each charge was worked and drawn in less than an hour, and was so thoroughly decomposed that only traces of aluminium phosphate were found in the insoluble portion. The chief reaction is the formation of a double silicate of alumina and soda and of trisodium phosphate, and may be represented as follows:—

$$AlPO_4 + 2\,Na_2SO_4 + 2\,C + SiO_2 = NaAlSiO_4 + Na_3PO_4 + 2\,SO_2 + 2\,CO.$$

This mass on analysis showed 30·92 per cent. SiO_2, 11·16 per cent. FeS, 27·46 per cent. Al_2O_3, 28·03 per cent. NaOH, and 2·40 $PO(OH)_3$. "By lixiviation in the ordinary vats of alkali-works a solution of trisodium phosphate is obtained. The insoluble residue is very easily washed, being coarse and open; it consists of the aluminio-sodium silicate, a little iron sulphide, sand, and cinders from the coal; it has absolutely no smell, either at first or in whatever atmosphere it may be kept" [this is considered a chief advantage of the process; but it is overlooked that the SO_2 escaping at the treatment in the furnace must cause both smell and other unpleasant consequences in a very striking manner. Close roasters do not seem at present to have been so much as tried]. "The solution of trisodium phosphate, coloured green by ferro-sodium sulphide, may be easily converted into the ordinary disodium phosphate by the addition of phosphoric acid [where is this to come from?]; or caustic soda can be made from it by means of lime, according to the equation

$$2\,Na_3PO_4 + 3\,CaO + 3\,H_2O = Ca_3(PO_4)_2 + 6\,NaOH.$$

The causticizing of a phosphate liquor can take place at higher densities than in the present process, say at sp. gr. 1·12, thereby saving some fuel. The calcium phosphate arising in this process only requires partially drying to make it fit for the market, and, as an 80-per-cent. article, fetches about £6 per ton. After causticizing, the liquor is worked in the ordinary way by evaporating and fishing, and the caustic soda carried to 'cream' or to fusion. Or else the trisodium phosphate is, by means of ground chalk, converted into carbonate, thus:

$$2\,Na_3PO_4 + 3\,CaCO_3 = Ca_3P_2O_8 + 3\,Na_2CO_3.$$

The above-mentioned insoluble residue, being quite innocuous, may be piled in heaps, the copperas formed by the oxidation of iron sulphide dissolved out, and the iron-free residue used for alum-making, sewage precipitation, &c." [Of course the "soda-alum cake" to be made out of this product could not be sold at a price leaving any thing whatever for the totally useless soda contained in it, amounting to one fourth of the total soda!]

17. *By means of calcium bisulphite.*—According to Gutzkow's American patent (No. 198293, Aug. 29, 4877), sodium sulphate precipitates calcium sulphate from a solution of calcium bisulphite. By distilling the solution of sodium bisulphite half of the SO_2 is liberated; the residual sodium sulphite, treated with caustic lime, yields caustic soda and again calcium sulphite.

B. *Soda from Sulphate after converting it into Sulphide.*

1. *By heating sulphate with coal.*—At a very early period a sulphide containing carbonate was thus obtained, which by lixiviating, boiling down, fishing out, and again calcining was made richer in corbonate. This process is describad in a notebook of Tennant's works, dating from 1800 (Mactear, p. 18). According to a paper of Mactear's in the 'Journal of the Chemical Society,' 1878, vol. ii. p. 476, Liebig proposed to the same firm, by a letter dated July 11, 1839, heating of sulphide with coal to 300° C. as the best of all soda-making processes; he stated that first oxalate and acetate were formed, and these on heating passed over into carbonate. Berzelius, Graham, aud Gay-Lussac approved the process: the latter made experiments on a large scale at Chauny; others were made at St. Rollox; but in neither case was success obtained. Liebig is said to have ascribed this to the fact that the decomposition takes place in another way than that which he had imagined at first, viz.

$$2Na_2SO_4 + 4C = Na_2CO_3 + Na_2S_2 + 2CO_2 + CO.$$

(This process will be referred to again at the end of Chapter VI.) On May 31, 1861, Laming obtained provisional protection for a process of mixing sulphate with some carbonaceous matter, heating the mixture in a furnace, and passing through it a current of steam and of air. When no more sulphuretted hydrogen is given off, the solid product is removed and the alkaline carbonate dissolved out and obtained in the ordinary way.

2. *By means of acetic acid.*—Sodium sulphide, obtained by heat-

ing sulphate with coal, according to Duhamel and Marggraf, is converted into acetate (p. 299), and this by drying and ignition into carbonate. This process only possesses historical interest.

3. *By means of calcium carbonate.*—This is Leblanc's process.

4. *By means of barium carbonate.*—G. Reinar (Wagner's Jahresb. 1858, p. 118, 1864, p. 167) proposed employing this in lieu of calcium carbonate for Leblanc's process in countries where native barium carbonate "occurs in very large quantities," in the proportion of 100 sulphate, 200 $BaCO_3$, and 75 bituminous coal. The residue from lixiviation, consisting of (hypothetical!) barium oxysulphide, hyposulphite, and carbonate, was to be worked for baryta salts. From the outset, as Hofmann ('Report by the Juries,' p. 32) justly says, it is not apparent what is to be gained by replacing calcium carbonate by a compound having more than thrice its atomic weight, entailing the heating and manipulation of a much greater weight and bulk of material, merely to obtain compounds less adapted than native barium carbonate for the preparation of other barium salts. [The ratio of the atomic weights, however, is strongly exaggerated here; the atomic weight of $BaCO_3$ is not "more than thrice" as much as that of $CaCO_3$, but as 197 to 100; and only this proportion, not that between the elements Ba and Ca, can be taken into account here.] Reinar's proposal is further vitiated by the same error which has rendered many other proposals in the "baryta industry" abortive, viz. the assumption that native barium carbonate occurs anywhere in "very large quantities," approaching those of limestone. The only known larger deposits near Hexham in Northumberland are already exhausted to a great extent; the price of any thing like a good quality, delivered at Newcastle, is at least ten times as much as that of limestone even in less favourably situated places. Moreover, in this special case Wagner (his Jahresb. 1858, p. 168), even when employing twice the quantity of barium carbonate, in experiments on a small scale, obtained very unsatisfactory results, especially very much sulphide in the liquors.

5. *By means of iron or ferric oxide with heat.*—We have already seen (p. 298) that Malherbe's soda-making process of 1778 is founded upon this principle. This process is also known as Alban's, because Alban carried it out as a manufacture. He fluxed sodium sulphate with coal to form sulphide, and added scrap iron; the mass of iron sulphide and caustic soda, formed

with the assistance of the oxygen in the fire-gas, was exposed to the air till it fell to powder, and then lixiviated. In 1828 F. E. Siemens, at Pyrmont, made soda on the large scale by a similar process; but he decomposed the Na_2S by a mixture of maganese peroxide and iron (Wagner's 'Regesten,' p. 36). This process forms the natural transition to that of E. Kopp, who changed the original process of Malherbe only so far as to add ferric oxide in lieu of metallic iron, which had first to be oxidized by the fire-gases. He certainly also aimed at utilizing the sulphur of the sulphate, of which Malherbe says nothing. The patent, taken out by Blythe and Kopp dates from October 3, 1855; and the process was actually at work for some time at the works of Messrs. Blythe and Benson at Church near Manchester. It was soon, however, given up again as useless. Kopp himself has described it at length (Ann. Chim. Phys. Sept. 1856, p. 21):—"125 kilog. dry sodium sulphate are mixed with 80 kilog. ferric oxide (for the first operations in the shape of native iron-ores, or smiths' scales, or even metallic iron, afterwards as recovered ferric oxide) and with 55 kilog. of small coal. In no case ought less than 5 parts Fe_2O_3 to be present to 9 parts of dry Na_2SO_4. The mixture is worked in an ordinary black-ash furnace; it exhibits about the same appearances as a batch of Leblanc black ash, and, in a fiery molten state, is drawn into an iron bogie, where it is covered and cooled, yielding a very dense evenly crystalline mass, of a coppery lustre on the surface. It cannot be lixiviated directly, because it swells up very much and yields green badly settling liquors containing much caustic and sulphide. But lixiviation is easy if the balls are first allowed to fall to pieces in the air under the influence of its oxygen and carbonic acid—still more so if cold moist carbonic acid (from a coke-oven) is admitted into a brick chamber, in which the balls rest on an iron grating, the powder falling through the same. A ball of 250 kilog. requires one cubic metre of space, 8 to 10 days' time, and about 10 kilog. coke for falling. Now, on lixiviating with water at 30° to 40° C., a perfectly clear solution of carbonate is obtained, along with a heavy precipitate consisting mostly of iron sulphide [and soda]. The liquor, without any boiling-down, yields very good soda crystals, or by evaporating to dryness and calcining can be converted into ash containing from 80 to 95 per cent. Na_2CO_3. The FeS is drained and pressed into bricks; if at all dry, it takes fire even below 100° C., and burns like tinder. It

is roasted on cast-iron plates, but better in a muffle; the SO_2 is conveyed into a vitriol-chamber, and the sulphuric acid made from it used for preparing sulphate; the residue of ferric oxide is employed over again in the first process. It contains still one third of all the soda employed; but this is not lost, as it is recovered on re-employing the ferric oxide. Only the mixing proportions must be altered in that case—say, to 125 kilog. sulphate, 140 kilog. recovered ferric oxide, 70 to 75 kilog. coal. The oxides of manganese or zinc may also be used, but less advantageously." Kopp represents the reactions thus :—

$$\text{I. } 2Fe_2O_3 + 3Na_2SO_4 + 16C = Fe_4Na_6S_3 + 14CO + 2CO_2;$$

$$\text{II. } Fe_4Na_6S_3 + 2O + 2CO_2 = Fe_4Na_2S_3 + 2Na_2CO_3.$$

On oxidizing $Fe_4Na_2S_3$ in the damp air and calcining, there are formed (leaving out the intermediate products) :—

$$\text{III. } Fe_4Na_2S_3 + 14O = 2Fe_2O_3 + Na_2SO_4 + 2SO_2.$$

Kopp's process was soon after thoroughly investigated by Stromeyer in his laboratory (Ann. Chem. Pharm. cvii. p. 333), and, on the whole, received a favourable judgment. He, however, entirely disagrees with Kopp's theoretical explanations, especially touching the part played by oxygen, the action of which is even injurious, especially by the formation of hyposulphite, overlooked by Kopp. The liquor obtained from the melted mass contains, beside sodium sulphide, hydrate and carbonate. Stromeyer states that the formula of the double sulphide arising in the process is $Fe_2Na_2S_3$ [Kopp, in Wurtz's Dictionnaire, ii. p. 1578, adopts the same formula, and thus gives up his own]; with water it forms a black jelly possessing extremely emulsive properties. It is decomposed by moisture and carbonic acid; and then with water a non-emulsive clear solution of almost pure sodium carbonate is obtained; the precipitate, however, always retains Na_2S in variable quantity. On treatment with CO_2 much H_2S is always given off; Kopp's second equation, therefore, cannot be right, and much sulphur must be lost. As the result of his many experiments, Stromeyer proposes only employing 1 molecule of Fe_2O_3 (80) to 3 of sodium sulphate (213); further, to work in furnaces with cast-iron bottoms, because the fluxing mass strongly acts upon fireclay, and to employ CO_2 as free as possible from oxygen.

Perhaps in consequence of Stromeyer's paper, and of the exact

description given by Kopp himself, this process excited much attention and raised far greater expectations of success than most other processes hitherto known. It was expected that in this way the sulphur, which in Leblanc's process is lost, could be continually reintroduced into the process. But already in 1863 (Report by the Juries, p. 31) Hofmann points out that Kopp's process, "although irreproachable so far as regards the conversion of sodium sulphate into carbonate [certainly not!], yet is very defective with respect to the reutilization of the sulphur; his sulphide of iron contains too much sodium sulphide to yield, when burnt, any considerable quantity of SO_2, which, moreover, is accompanied by an enormous bulk of nitrogen, corresponding to the oxygen combining with the iron and the sodium sulphide. Its utilization in vitriol-chambers would be out of the question." Kopp (*apud* Wurtz) reproduces Hofmann's judgment on referring to his own process without any remark, and thus makes it his own, adding that since the discovery of processes for recovering sulphur from tank-waste the motive for his process had ceased to exist.

According to experiments made by Waldeck (Dingl. Journ. cxcii. p. 417), not only fireclay, but also cast-iron, which Stromeyer had recommended for the furnaces, is acted upon "in a truly frightful way;" nor could lining the crucibles with a mixture of powdered coke and tar protect them. The original percentage of iron in the mixture is increased fourfold by that action. Even this would make Kopp's process practically impossible; but another point must be regarded, which is only incidentally touched upon by Waldeck when stating that the yield of soda from the fluxed mass was only 9·4 per cent. instead of 36 per cent. The author of this work, who in 1865 made a long series of experiments with Kopp's process in a furnace specially built for the purpose, came to the conclusion that the process was impracticable, because not merely does one third of the soda always remain in the insoluble residue, as admitted by Kopp himself, but, under the ordinary conditions of a reverberatory furnace, the re-formation of sulphate in the batch cannot be avoided; owing to this, the conversion of the sulphate into carbonate is so incomplete. Experiments in closed crucibles succeeded better. In this case 95 per cent. carbonate could be obtained; but the yield was always bad. The treatment with CO_2 had always to take place as much as possible in the absence of air; otherwise very much hyposulphite was formed.

In spite of its notorious failure, Kopp's process was for a long time (and in some treatises published only quite recently it is still) stated to be a most hopeful one, which might possibly drive Leblanc's out of the field—and this, although the only important advantage claimed for it over that of Leblanc, viz. the recovery of the sulphur, was already denied by Hofmann and given up by Kopp himself. Looking at the extremely bad yield and the destructive corrosion both of fireclay and iron by the fluxing mixture, no future can be predicted for Kopp's process.

A modification of the ferric-oxide process, returning to some extent in the direction of Malherbe's, was patented by Bowron and Robinson on December 3, 1863. "First sodium sulphide is to be made, and then ferric oxide introduced." The principal intention was that of making the more valuable caustic soda. The author, who had to conduct the trials for carrying out this process on a manufacturing scale, convinced himself of its uselessness. Whatever conditions of work might be observed, there always remained a large quantity of sodium sulphide undecomposed. This could be removed by boiling with MnO_2; but it only changed into hyposulphite, which cannot be separated from caustic soda by crystallization. The removal of the hyposulphite by barium chloride (Robinson's patent of October 31, 1865) proved quite impracticable. Besides, a great deal of sodium sulphate and carbonate, and in the residue much undecomposed sulphide, were present; the latter, as in Kopp's process, was to be turned to use by burning and employing the residue again; but this failed, from the same causes.

Macfarlane (Wagner's Jahresb. 1864, p. 171) ignites dried copperas with salt in a current of air; chlorine escapes, and a mixture of sodium sulphate and ferric oxide remains, which is mixed with coal and worked up as in Kopp's process; the hearth employed is of quicklime mixed with slightly basic slags and impregnated with sodium sulphide by melting a mixture of sulphate and coal upon it. The batch is treated as in Kopp's process; the remaining sulphide of iron is oxidized to copperas in moist air [which, it is well known, only takes place very incompletely]; and this is employed again for calcining with salt. Hargreaves and Robinson (patents of October 10 and 15, 1872) add to Leblanc's mixture ferric oxide, flux it in crucibles with holes in the bottom, lixiviate the mass, oxidize by exposure to the air the iron sulphide formed, and extract the product by hydrochloric acid. On March 3, 1873,

they patented mixing sulphate and coal with a salt of iron, manganese, or zinc, heating up to the formation of a coherent, porous, not fluxed lump, dissolving out the soda, burning the sulphides into oxides, and using them as above.

6. *By means of carbonic acid.*—Gren had made the observation that an aqueous solution of sodium sulphide is converted into carbonate by carbonic acid gas, with evolution of sulphuretted hydrogen if the introduction of CO_2 is continued up to the formation of sodium bicarbonate. Attwood, on June 22, 1819, obtained an English patent for this process. Pelletan in 1829 made soda in a works at Paris by this process; and Dumas explains it in detail in his treatise on applied chemistry, 1829. Gossage proved (in 1838) that CO_2 decomposes its equivalent of Na_2S; and in 1861 he reverts to this in his 'History of the Soda Manufacture,' p. 22, stating that in future the H_2S would be absorbed by ferric oxide, and the product employed for making sulphuric acid. The working out of this idea (which he had failed to accomplish himself in the intervening twenty-three years!) he wished to leave to younger men. Endeavours in this direction have certainly not been wanting. Wagner quotes (Regesten, p. 37) patents taken out by Beringer (1847), Newton (1853), Hunt (1861), Reissig (1865). He thought that with the introduction of ferric oxide as an absorbent for sulphuretted hydrogen this gas had ceased to be a source of inconvenience to the works and in their vicinity. How unfounded this opinion is we shall see in the Chapter on the utilization of tank-waste. Apart from the methods to be mentioned there for utilizing sulphuretted hydrogen (burning into SO_2 or S, mixing with SO_2, absorption by $Fe_2(OH)_6$), some proposals in this respect have been made with a special view to soda-making. One of these, contained in Gibb and Gelstharpe's patent for utilizing the copper in pyrites-cinders (comp. Vol. I. p. 613), has been so far successful that in fact Na_2S was decomposed by CO_2, and the H_2S was completely utilized for precipitating copper-liquors; but, in the first place, this process was from the outset restricted to the comparatively rare connexion with wet copper-extraction; and, secondly, it has had to be given up for this as well.

A great deal was expected in Lancashire of Hunt's patent (May 5, 1860). He asserted that he had found the decomposition of sodium sulphide to take place better than in solution, if the Na_2S was put, in pieces, on the perforated false bottoms of vessels, through which steam and CO_2 (generated by igniting chalk in

retorts) was conducted. By combining several vessels, the CO_2 was to be completely spent and strong H_2S obtained, which was to be mixed with air, ignited, and employed for vitriol-making. This process was tried, among others, in the works of Mr. Shanks at St. Helens. The CO_2 was there made from limestone and hydrochloric acid; and the H_2S was not dealt with at all, which sufficiently proves the experimental character of those trials. The peculiarity of Hunt's process, the treatment of sodium sulphide in *lumps* with CO_2, is not essential; that even a *solution* of Na_2S is completely and comparatively easily decomposed by CO_2 the author has himself seen at the works managed by Mr. Gibb; and the drawback observed there, that any oxygen remaining along with the CO_3 caused the formation of hyposulphite and consequently a loss of available soda, must equally have occurred in Hunt's process.

More modern patents upon this process, containing nothing essentially new, have been taken out by Verstraet and Oliver (Aug. 13th, 1862; to the solution of Na_2S milk of lime is to be added in order to lessen the tendency to the formation of hyposulphites), Claus (Sept. 7th, 1869; he employs blast-furnace gases, along with the CO_2 produced in reducing the Na_2SO_4), Young (Oct. 10th, 1872; he employs a boiling solution of Na_2S), Fletcher (May 16th, 1873; he proposes employing the SO_2, generated by burning the H_2S, for Hargreaves's sulphate process), and Prache (1873; he, like many before him, conducts the H_2S into water in which hydrated ferric oxide is suspended, which is afterwards regenerated by exposure to the air; or the CO_2 can be directly passed into a mixture of sodium sulphide and hydrated ferric oxide). Wallace and Claus (July 25th, 1877) decompose alkaline sulphides by the gases escaping on saturating with acids the ammonia-liquor of gas-works (*i. e.* a mixture of CO_2 and H_2S). Thus pure H_2S is formed, which is burnt into SO_2 or used for precipitating As, Cu, Ag, or Pb. Some other modifications are also described, but all of them founded upon the employment of gas-liquor; so that this, not the alkaline carbonates, is the principal consideration.

H. B. Condy (April 19th, 1877) employs crystallized sodium sulphide with 67 per cent. water, which is treated with CO_2 in a closed space on a perforated bottom; by the liquefaction of the water of crystallization a solution of sodium carbonate and bicarbonate is formed; the H_2S is absorbed or burnt according to any one of the known plans.

As a special *prescription for preparing sodium sulphide,* Arrott (patent June 3rd, 1859) proposes melting 4 parts of sodium sulphate with 1 part of coal in a cupola, which of course is heated by special fuel. Laming (like many others) ignites 2 parts of sulphate with 1 part of coal in a closed vessel. Gossage (patent of Nov. 18th, 1859) employs the same proportions, but in a close roaster, in order to exclude reoxidation. Fifty parts by weight of slack per cent. of sulphate, or 33 per cent. of powdered coke, is to be taken, the mass to be constantly stirred, but the heat not increased up to the fluxing of the mass; the CO_2 arising in the process is to be sucked away by a fan-blast or similar apparatus, and employed for decomposing the sodium sulphide. The batch must be drawn as quickly as possible, and protected from the air. Wilson (patent of June 3rd, 1859) fluxes a mixture of 4 cwt. sulphate, ¼ cwt. of barium sulphate, and 2½ cwt. small coal or 2 cwt. coke powder in an ordinary reverberatory furnace, or, still better, in a revolving cylinder furnace, in which less heavy spar need be used, as the air has less access, than in a furnace worked by hand. (Also Jean, Monit. Scient. 1869, p. 1007, proposes making Na_2S by the help of heavy spar, but employs a very great deal of it, viz. 25 kilog. sodium sulphate, 75 kilog. barium sulphate, 10 kilog. charcoal dust, and 15 kilog. coal dust; the operation takes place in an ordinary black-ash furnace which is said not to be corroded by this mixture.) Wilson further describes an apparatus for running melted sulphate through a column of coals or coke at a cherry-red heat, in order to convert it into sulphide. A laterally attached deep furnace supplies the necessary heat as a gas-generator; the sulphate is charged onto the top of the coke-column, on a perforated arch, and there fuses of its own accord; the gases afterwards travel through a tower filled with continually moistened pebbles in order to cool the CO_2 and return any sodium salts carried away; at the end of the apparatus a fan-blast causes the movement of the gases and the air throughout the whole apparatus. The CO formed at the same time is burnt in the upper portion of the tower by air admitted for this purpose. The CO_2 is then employed for making carbonate from the sulphide, or else for turning carbonate into bicarbonate, which is itself employed for converting sulphide into carbonate.

It is very probable that such an apparatus would be destroyed after a short lapse of time. A similar process was patented by Claus (Sept. 7, 1869), who attempted to preserve the cupola in which the reduction of the fused sulphate takes place by means of

a water-jacket. The sulphide is partly tapped off at the bottom in a fluid state; but a great part is volatilized and is passed along with the products of combustion into a scrubber, through which a solution of sodium sulphide is run down; in this the volatilized portion is condensed and at the same time converted into carbonate by the carbonic acid formed in the reducing process. Another proposal by Claus refers to the manufacture of sodium or potassium sulphide by means of gaseous fuel, carefully kept free from uncombined oxygen, so that but very little hyposulphite can be formed. A third proposal is this—to make barium sulphide from barium sulphate, dissolve it in water, and decompose a solution of sodium sulphate by the same, when sodium sulphide will be formed and barium sulphate be recovered. This process (which is far too expensive to be of practical importance) was once more proposed, as new, by Vincent (Compt. Rend. lxxxiv. p. 701). Willans (patent of Feb. 4th, 1860) proposes making Na_2S from sulphate without mixing it with coal, merely by the action of CO and steam in a red-hot furnace.

The process with sodium sulphide and carbonic acid has been most thoroughly worked out by the celebrated inventor of the manganese-recovery process, Walter Weldon, who spent years upon it and believed he had attained his object, when, on Aug. 28th, 1876, and Feb. 2nd, 1877, he took out a series of patents in reference to it. His process commences with a very original way of making the sodium sulphide. Sulphate, made in any suitable way, is fused in a Siemens's regenerative furnace; and the combustion-gases of this furnace are at the same time employed in a second furnace, in which the sulphide is made. The first furnace is placed at such a height that the fused sulphate can run into the manhole of the second furnace. This second furnace, in which the sulphate is reduced to sulphide, is the principal thing. It is a revolving cylinder furnace such as are now generally used for the ordinary black-ash process. [When trying the process on the large scale no revolving furnace was employed, owing to the great cost, but a hand-furnace; in case of success revolvers would have been used. In his last patent Weldon reverts to the use of a hand-furnace exclusively.] As all brick-work and iron is extremely strongly corroded by melting sodium sulphide, the furnace had to be lined with a more refractory material. As such, bricks made of powdered coke with a little tar, moulded with a very strong pressure, and heated to a red heat in a close furnace are used; they are set in a

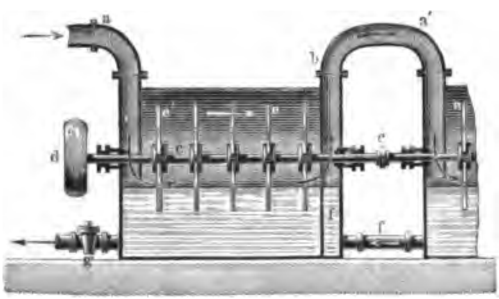
mixture of the same materials. This lining has turned out entirely successful in practice, so long as the fire-gases were free from oxygen. That end of the furnace through which the fire-gases enter can be closed air-tight. For this purpose the "eye," always hung in cylinder furnaces between the fireplace and the cylinder [comp. Chap. V.], is so arranged that it can be moved aside instanter and a solid disk of the coke mixture can be put in its place; the latter is surrounded by an iron ring carrying a broad flange, which is firmly connected by bolts with the central opening of the cylinder; thus the disk revolves with the cylinder, and forms an air-tight closing. The outlet-hole, at the other end of the cylinder, is continued into a fire-flue, which is divided into two parts, so that by suitable dampers the gases can either be taken to the chimney or the carbonic acid gas can be kept for special use in suitable apparatus or employed directly. Also the furnace from which the cylinder furnace is supplied with fire-gases, be it the sulphate-melting furnace or a special gas-producer, is so arranged that the products of combustion can either be conveyed into the cylinder furnace or elsewhere. Now, in the converter, small coke or charcoal [according to the patent of Feb. 2nd, 1877, exactly as much as suffices for forming carbonic acid with the oxygen of the sulphate, viz. 16·9 per cent. of the weight of the sulphate, of course adding the impurities; it is then best to work in a blind roaster and to aspirate the carbonic acid gas by means of a fan-blast] is brought to a red heat, by admitting fire-gases at one end and allowing them to escape at the other end; then the fire-gas is cut off, the entrance-opening closed in the above-described manner, and the exit-opening connected with the apparatus for keeping or employing the carbonic acid; from the furnace, placed higher up, fused sulphate is run onto the red-hot coke or charcoal; and the two are mixed by quick revolutions of the cylinder. The reaction between sulphate and coal thus goes on in a vessel which during this period has only one opening, that for removing the carbonic acid. Weldon has also constructed another, simpler, not revolving furnace for the same object. If the sulphate and the coke have each been sufficiently heated, the reaction between them will be finished without applying any ulterior source of heat; otherwise fire-gas must be again admitted, and in the meantime the other end must be connected with the chimney. Of course, if the carbonic acid is not to be utilized, the exit-gases may always be allowed to go into the chimney.

The sodium sulphide may now be mixed with silica or alumina in the state of powder and decomposed by superheated steam in the cylinder furnace itself or in another furnace, during which time the other end of the furnace must be connected with the apparatus for burning or absorbing the sulphuretted hydrogen, after cooling and condensing the water; sodium silicate or aluminate remains behind. (This part does not seem to have been seriously carried out on the large scale.) Or else the sodium sulphide is treated with carbonic acid in the following way. The sulphide is run into air-tight iron boxes lined with coal, and after sufficient cooling lixiviated with exclusion of air. The liquor is made so strong as to contain at least 12 per cent. Na_2S; but it is better to make it quite saturated, so as to contain 17 to 20 per cent. Na_2S. The solution is then treated with carbonic acid in a methodical way, in a set of six closed vessels. The liquor only half fills these vessels; and by a mechanical agitator their upper halves are constantly filled with a spray; there are also several partitions reaching down from the cover nearly to the level of the liquid, so as to force the gases to travel in a circuitous route. By means of a suitable system of cocks and pipes, gas can be admitted into the upper part of each vessel, and conveyed through all the other vessels in succession. In this way the complete decomposition of the sodium-sulphide liquor in the first vessel can be attained, and at the same time the gas issuing from the sixth vessel consists of practically pure sulphuretted hydrogen. When the liquor of the first vessel is sufficiently decomposed, it is run off, fresh liquor is run in, and the second vessel is now made the first, the sixth fifth, the first sixth with respect to the current of gas, and so forth. Instead of this the gas may also be passed through the vessels always in the same succession; but then the liquors, after completing the decomposition, are run from one vessel into the other in the opposite direction. This, however, can only be done if the decomposition is not carried so far as to precipitate bicarbonate in a solid form. Usually the operation is so conducted as to obtain as large a separation of crystals as possible, and, for this reason, at the ordinary or only a slightly raised temperature, both of the liquor and of the carbonic acid. In this way up to 80 per cent. of the soda can be obtained as a precipitate of bicarbonate; the impurities consequently remain in the mother liquor, which is washed off with a cold saturated solution of bicarbonate, whereupon the residue is brought into

saleable form either as bicarbonate or as alkali. The mother liquor is again employed for dissolving sodium sulphide, till it has become too much charged with impurities. It is much better not to carry on the operation till all the sodium sulphide is decomposed, because this can only be done by a large excess of carbonic acid; the mother liquor containing sodium sulphide can be easily employed for dissolving a fresh batch. The treatment is accordingly only continued till at least 50 or at most 80 per cent. of the sodium sulphide has been decomposed. If the treatment does not take place in the cold, but at a higher temperature, instead of bicarbonate sesquicarbonate is obtained, which on the cooling of the liquid crystallizes out. If the sulphide contains polysulphides, it is necessary to work with dilute liquors, so that the sulphur can settle down.

The construction of the absorbing vessels is more clearly shown by the section, fig. 162: *a a'* are entrance-pipes for the gases,

Fig. 162.



reaching down nearly to the surface of the liquid and nicked out at the bottom; *b*, exit-pipe; *c*, a shaft revolving in glands *above* the liquid, driven by the pulley *d*, and carrying the agitating blades *e e*; *f*, connecting pipe for the liquid; *g*, running-off cock for the same. The vessels may be made of iron, covered with hard pitch, or of hard wood, if the sodium-sulphide liquor is to be treated cold, but of iron covered with lead or stone flags if at a higher temperature. Similarly the agitating shaft is protected from the effect of the sulphide by a coating of pitch or iron. The agitating paddles best consist of hard wood.

It remains to deal with the sulphuretted hydrogen gas which is given off on the treatment of the Na_2S in the furnace itself with

superheated steam, or on that of its solution with CO_2. For this the process patented by Weldon on July 31st, 1871, is to be employed. It consists in bringing the gas into contact with a metallic oxide suspended in water, hydrated ferric oxide being the best (compare also Lunge's patent of April 20th, 1866). This treatment is to take place in an apparatus quite similar to that serving for the introduction of CO_2; so that the gas is introduced on the top of the first of six vessels in which the metallic oxide suspended in water is constantly splashed about by a paddle-wheel, and escapes out of the sixth vessel completely deprived of its H_2S. When the metallic oxide in the first vessel is entirely converted into a sulphide or a mixture of a sulphide with sulphur, the contents of the vessel are drawn off, those of the second vessel are run into the first, those of the third into the second, and so forth; the sixth vessel, which gets emptied, is charged with a fresh mixture of oxide and water. The mixture run off from the first vessel and saturated with H_2S is treated with a strong current of air in an oxidizing-tower similar to those used in Weldon's manganese-recovery process; this converts it into a mixture of hydrated ferric oxide and sulphur, suspended in water, which can be employed directly in the absorbing-vessels; but when it has become very rich in sulphur, it must be kept separate, and either by dissolving the iron in HCl the sulphur obtained as such, or the whole must be dried and the sulphur burnt.

These processes were carried out on a pretty large scale by a company founded for this purpose, but, in spite of all exertions, have now been given up as impracticable. The reason stated for this is that pure sodium sulphide, entirely free from polysulphides, hyposulphites, and caustic, such as was recovered in Weldon's furnace, turned out entirely infusible and could not be got out of the furnace; if, on the other hand, some air was admitted in order to form a little of those compounds and thus to make the mass fusible, the carbon lining of the furnace was quickly burnt and repairs were incessantly required. Whether these difficulties can be overcome by new modifications the future will show. Wallace and Claus, on July 25, 1877, patented "bauxite" (see p. 333) as a lining for furnaces in which alkaline sulphates are reduced.

7. *By means of sodium bicarbonate.*—Wilson on Feb. 25th, 1840, patented the decomposition of sodium sulphide and bicarbonate into monocarbonate and sulphuretted hydrogen, thus:

$$Na_2S + 2NaHCO_3 = 2Na_2CO_3 + H_2S.$$

A solution of 48 parts sodium sulphide is to be boiled with 85 parts dry sodium bicarbonate, the H_2S collected in a gas-holder and burnt in order to be converted into sulphuric acid in vitriol-chambers. Although the bicarbonate has to be made from finished carbonate, the process is not quite so irrational as it appears at the first glance; for the bicarbonate can be made with impure CO_2 (containing air), and the H_2S is still obtained quite pure and free from other gases. On the contrary, some prospect would be opened in the future for this process, if a simple plan for advantageously disposing of sulphuretted hydrogen should be discovered. On Feb. 5th, 1853, Werckshagen patented the same process; he proposes to make sulphur from the H_2S by bringing it into contact with SO_2 and steam. Böhringer and Clemm on April 19th, 1853, again patented the same thing, also with the proposal to decompose H_2S by SO_2. Otto certainly could not find an easy method for completely decomposing sodium sulphide by bicarbonate (Lehrbuch der Chemie, 4th ed. ii. 2, p. 341). Both Wilson and Gossage include this process in their patents of 1858 (see above).

8. *By means of alumina.*—Wagner (in his Jahresbericht, 1865, p. 332) proposes to employ, instead of carbon dioxide, the much more active alumina (from bauxite or cryolite) for expelling the sulphur from Na_2S, by boiling it with a solution of the latter. The H_2S is to be absorbed by Laming's mixture or ferric chloride, and the sodium aluminate converted by CO_2 into carbonate and aluminium hydrate. This method seems never to have been tried anywhere. If the alumina really acted simply and easily, it would also furnish pure H_2S; but it does not look very promising.

A modification of this process was patented by Siermann (German patent, No. 3280, Jan. 1878). Sodium sulphate and alumina are ground up together, leaving a slight excess of the former, and heated in an iron muffle completely surrounded by fire, allowing the air to enter as soon as the mass has attained a bright-red heat. Sulphur dioxide is given off and collected in a chamber common to several muffles, which are charged alternately so as to produce a uniform current of SO_2, which is conveyed into vitriol-chambers. The residue in the muffle, consisting of sodium aluminate, is drawn out, lixiviated with water, and carbon dioxide passed through the solution till it has been decomposed into a precipitate of aluminium hydrate and a solution of sodium carbonate. The former is used over again

in the first part of the process. The carbon dioxide is best supplied by the fire-gases from the muffle-fire, which is for this purpose fed with coke.—This process is any thing but a cheap one: the sodium sulphide will play great havoc with the iron muffles; and the gas evolved will hardly be converted into sulphuric acid with any pecuniary profit.

9. *By means of ammonium carbonate.*—Laming (patent dated Nov. 17th, 1859) proposed a number of different ways for making sodium carbonate from sulphide by means of ammoniacal gas-liquor. The principal being in all the same, it will suffice to describe one of these plans. Sodium sulphide is moistened with strong ammoniacal liquor (*i. e.* mostly ammonium carbonate and sulphhydrate), and heated to dryness in a retort at a temperature of 150° C.; ammonium sulphhydrate volatilizes; and from the residue in the retort sodium carbonate is extracted by lixiviation. The ammonium sulphhydrate is conducted through a porous mass containing hydrated iron oxide; here it leaves its H_2S; and pure NH_3 escapes, which by treatment with carbonic acid gas is reconverted into ammonium carbonate.

10. *By means of magnesia.*—Clemm (French patent, Oct. 6th, 1853) proposes mixing a concentrated solution of sodium sulphide with neutral magnesium carbonate and heating to 300° C. Or 1 equivalent of common salt is decomposed by 2 equivalents of kieserite (anhydrous magnesium sulphate); by this a double sodium-magnesium sulphate is formed, mixed with $MgCl_2$; this is evaporated to dryness, ignited till the latter has been decomposed into MgO and HCl, 25 to 30 per cent. coal added to the residual mixture of the double salt and magnesia, and the mass heated on a hearth made of magnesite. Hereby SO_2 escapes and is worked for vitriol. The porous mass is allowed to cool in closed vessels; it contains sodium sulphide, magnesia, soda, and an excess of coal. It is treated with CO_2, in order to expel the H_2S, and at last heated to 300° C. in order to drive off all the sulphur.

11. *By means of copper, zinc, or lead oxide.*—Already on Nov. 22nd, 1804, Clayfield obtained a patent for treating sodium sulphide with lead or zinc, or their oxides, for the purpose of alkali-making. Prückner in 1829 gained a prize offered by the St.-Petersburg Academy of Sciences by the following process:—Sodium chloride with ammonium sulphate are decomposed into sodium sulphate and ammonium chloride. By ignition with coal the sulphate is reduced

to sulphide; and its solution is boiled with coppersmiths' scales (Cu_2O) till all the sulphur has been precipitated as copper sulphide and only caustic soda remains. The former, by gentle roasting, is converted into cupric sulphate, or more strongly heated till only CuO remains; the escaping SO_2 is conducted into ammonia-liquor, obtained by heating the ammonium chloride of the first operation with lime. The ammonium sulphite remains in contact with the air till it has been converted into sulphate, and can serve for again decomposing common salt. The caustic soda is used as such, or, by evaporating with coal dust and igniting, converted into carbonate (!). On December 9th, 1839, Poole for some anonymous individual obtained a patent for an exactly similar process; but he converts his caustic in a more rational way into carbonate (if such a conversion can be called rational at all), viz. by a current of CO_2 in a tower filled with pieces of granite. The ammonium sulphite is oxidized by exposing its solution for a sufficient time to a current of air in a vessel filled with wood shavings, analogous to a vinegar-making tub. Directly after (on Jan. 21st, 1840), Hunt patented the same method in a slightly different form. Sodium sulphide, obtained by heating sulphate with one third of coals, is dissolved and treated with a mixture of $20Cu_2O$ (obtained by decomposing Cu_2Cl_2 with lime) and 1 metallic copper; so that caustic soda and copper sulphide are formed. The latter is gently heated in order to obain cupric sulphate, which is decomposed with NaCl into $CuCl_2$ and Na_2SO_4; the $CuCl_2$, being digested with finely divided copper, is converted into Cu_2Cl_2, which, owing to its insolubility, is easily separated from the solution of sodium sulphate. Instead of CuO, ZnO may be employed for desulphurizing, which may take place altogether as stated on p. 356. The metallic sulphides may also be more strongly roasted, and the arising SO_2 utilized in vitriol-chambers.

Possoz (Compt. Rend. xlvii. p. 848) takes up the proposal of Prückner (also advocated by Persoz), principally in order to employ the caustic soda for making oxalic acid from sawdust according to his method. Possoz found that the suboxide, Cu_4O, is more suitable than the protoxide, Cu_2O, because, on using the latter, part of the sulphide is converted into sulphate and hyposulphite. Johnson, on May 6th, 1862, again patented (for Burton) the desulphurization of Na_2S by Cu_2O (or Fe_2O_3); even later Parnell obtained a patent for employing zinc oxide; and on April 3rd, 1876, Bazin and Wilden

obtained a French patent simply for making caustic soda from sodium sulphide and cupric or ferric oxide.

M'Clintock, on October 28th, 1861, obtained provisional protection for the following process :—Seven parts sodium sulphate are fluxed with 8 parts copper oxide and 3 to 3½ parts coals; from the mass sodium carbonate is to be dissolved out, the remaining copper sulphide to be calcined to oxide, or regulus, or sulphate, &c.

12. *By means of ferric or manganic oxide in the wet way.*—Arrott on June 3rd patented the following process:—A quantity of peroxide of iron or oxide of manganese is put into a solution of caustic soda, and the solution is evaporated and heated until the whole has assumed an olive-yellow colour. Water dissolves out from this mass caustic soda, leaving the oxide now in a state to take sulphur from the sodium sulphide. A solution of this is now added so long as the oxide continues to take up sulphur, whereby a solution of caustic soda and a precipitate of FeS or MnS is produced. The weight of the metallic oxide must at least equal that of the Na_2S. The oxide, caustic soda, and solution of sodium sulphide may be added together. Caustic soda is obtained by heating together carbonate of soda and peroxide of iron or manganese to a full red heat for two or three hours and lixiviating the residue.

Gossage (patent of Nov. 18th, 1859) mixes a solution of sodium sulphide with ferric oxide, and injects a current of carbonic acid by means of a forcing-pump; or he decomposes sodium sulphide by sodium bicarbonate or sesquicarbonate in the presence of ferric oxide. Iron sulphide is precipitated, which is either dried and burned for the production of sulphuric acid or fluxed with common salt with access of air to form sulphate.

Wilson (patent of Nov. 22nd, 1838) treats a solution of sodium sulphide with hydrated iron protoxide, and passes steam through the mixture. The $Fe(OH)_2$ is obtained by precipitating $FeCl_2$ with milk of lime, the $FeCl_2$ by boiling copperas solution with common salt, in which case anhydrous sodium sulphate is precipitated. The copperas is recovered by treating the FeS with sulphuric acid, burning the H_2S, and making from it sulphuric acid again (!).

13. *By means of native carbonate of iron.*—Habich (Dingl. Journ. cxl. p. 370) proposed this at first for desulphurizing ordinary black-

ash tank-liquor, and afterwards as a soda-making process. But that mineral, according to the unanimous testimony of practical men, can do neither the one nor the other, as it acts too slowly and incompletely. The same process had been already patented in England by Cottrill (Jan. 11th, 1853). In France, De la Souchère patented it again in 1878.

All attempts to make caustic soda from sodium sulphide by means of metallic oxides have hitherto been foiled by certain drawbacks. First, it is next to impossible to make sulphide free from carbonate, which weakens the caustic. Secondly, much more than an equivalent of the oxide must always be employed for decomposing the sodium sulphide completely—frequently many times the equivalent. Thirdly, the recovery of the oxide from the metallic sulphide is always a costly operation, which alone swallows up all possible profit as against the ordinary process—in spite of the utilization of the sulphur, which is always very imperfect, often economically impossible. Lastly, it is impossible to avoid a certain loss of the metal, which entirely excludes copper and even lead, considering its high atomic weight; and the loss is too great even for the cheaper metals.

14. *By means of sodium silicofluoride.* (Claus, patent dated Dec. 27, 1869).—Equivalent quantities of these compounds are heated by steam in a closed vessel. The reaction is :—

$$Na_2SiF_6 + 2Na_2S + 2H_2O = 6NaF + SiO_2 + 2H_2S.$$

The H_2S is collected and utilized in some manner. The residue, consisting of a solution of sodium fluoride and of silica, is, by treatment with calcium hydrate or carbonate, converted into $NaOH$ or Na_2CO_3 and CaF_2. The latter is mixed with the silica, treated with HCl, and then with $NaCl$; sodium silicofluoride is regenerated, as well as HCl, which can be obtained by distillation. Even the chlorine of the $NaCl$ can be utilized if, instead of lime, magnesia be employed for decomposing the sodium fluoride. According to direct information from Mr. Claus, the reactions of this process are both quick and complete.

III. The Manufacture of Soda from Cryolite,

being a really carried-out branch of industry, will be described in a special chapter (XVII.).

IV. The Manufacture of Soda from Nitrate of Soda.

All the sodium nitrate which is required for the manufacture nitric acid or directly used in vitriol-works is converted into acid sulphate (nitre-cake); and a large quantity of this is employed in alkali-making. There exist, however, a series of proposals for the direct utilization of nitrate in the alkali-manufacture.

1. *By means of coal,* by deflagration and lixiviation of the residue. —Duhamel (1735) was already aware of this reaction; Marggraf (1762) confirmed it; and Leuchs in 1844 still thought it applicable if nitrate was cheap enough! (Wagner's 'Regesten,' p. 55).

2. *By means of manganese peroxide.*—Wöhler showed (1861) that on igniting sodium nitrate with MnO_2 without access of air the nitric acid is completely decomposed and a mixture of caustic soda with a lower oxide of manganese remains behind; not a trace of sodium manganate is formed (Ann. Chem. Pharm. cxix. p. 375).

3. *By means of potassium carbonate.*—Leuchs seems to have been the first to propose making potassium nitrate and sodium carbonate by mutually decomposing chemically equivalent quantities of sodium nitrate and potassium carbonate. Anthon (1840) found this method to answer very well. Gentele (Dingl. Journ. cxviii. p. 200), Kuhlmann (Bull. Soc. d'Encourag. 1859, p. 567), Bolley (Dingl. Journ. clv. p. 418), Wöllner (Polyt. Notizbl. 1860, p. 49), Schnitzer (Dingl. Journ. clxii. p. 132), Schwarz (ib. clxiii. p. 314), and Grüneberg (ib. clxvi. p. 75) give explicit details on this process. Grüneberg seems to have been the first who, during the Crimean war (1854–55) and subsequently, manufactured potassium nitrate and sodium carbonate by this now abandoned process. Also the manufacture of potassium nitrate by means of caustic potash, with caustic soda as a by-product, belongs here (described by the author in Dingl. Journ. clxxxii. p. 388); but in all cases the potassium nitrate is the principal product, and soda only a by-product, while in the patent of De Sussex (June 29th, 1846) it was proposed to decompose common salt by nitric acid and then convert the sodium nitrate into carbonate!

4. *By means of magnesium or calcium sulphate.*—Kuhlmann (Compt. Rend. lv. p. 246) showed that sodium nitrate on being ignited with the above salts is converted into sulphate, whilst nitrogen tetroxide escapes, which on being brought together with air

and water regenerates nitric acid. Thus sodium sulphate would be made along with nitric acid [but at a great loss of the latter].

5. *By means of silica or alumina.*—Already in 1648 (Wagner's 'Regesten,' p. 56) Glauber knew that on igniting a mixture of saltpetre with clay &c. nitric acid was expelled. Latterly attention has been drawn again to the fact of nitrate being decomposed by silica (Reich's saltpetre test, Dingl. Journ. clx. p. 357) and alumina (Wagner, in his 'Jahresbericht,' 1865, p. 250); thus sodium silicate or aluminate might be obtained, and by CO_2 converted into soda, recovering SiO_2 and Al_2O_3. Of course an indispensable condition is the complete recovery of the nitric acid from the nitrogen oxides, which is said to be carried to 90 per cent. in the works making arsenic and phthalic acids, but according to Lieber (see below) is very difficult in the above cases. For that reason the process has nowhere found a home, although it was patented for England on Aug. 6th, 1866, by Newton for Baker, Poole, and Stace; they wanted to employ the recovered nitric acid for decomposing common salt; this, however, is not practicable, as "euchlore" is formed in this process.

6. *By means of calcium carbonate.*—Walz (Wagner's Jahresb. 1869, p. 182) heats sodium nitrate with calcium carbonate and steam in retorts, condenses the nitric acid, of which almost (?) the theoretical quantity is obtained, and utilizes the residue, consisting of sodium carbonate and lime, either directly or after lixiviating with cold water, for making caustic soda. Exactly the same thing was patented in Prussia by Lieber in 1867 (Deutsch. chem. Ges. Ber. viii. p. 49); after nine mouths' working he was obliged to give up the process, owing to the strong corrosion of all the vessels.

7. Hargreaves ('Mechanics' Magazine,' 1868, p. 186) obtains soda from the slags produced in his (abandoned) *process for converting pig-iron into wrought-iron or steel by means of sodium nitrate.*

8. *By means of iron or other metals.*—Pollacci (Chem. News, xxvi. p. 288) heats a mixture of sodium nitrate with two or three times its weight of iron wire in an iron crucible or retort to a red heat; the mass is lixiviated with water: caustic soda is dissolved; and ferric oxide remains behind:

$$10Fe+6NaNO_3=3Na_2O+5Fe_2O_3+6N.$$

Wöhler (Ann. Chem. Pharm. lxxxvii. p. 373) employs cut-up copper foil for the same purpose. Neither of these processes has any practical interest. Heard, on Aug. 1st, 1838, patented melting lead with sodium nitrate, treating the product with CO_2 in closed vessels, and separating the soda from the white lead by lixiviation. Hill (Chem. News, xxvii. p. 170) points out that solutions of sodium nitrate at a high temperature are converted by zinc into caustic soda, ammonia, and hydrated zinc oxide; this could only become of technical importance, even with the present high prices of ammonium salts, if the problem were solved of recovering the zinc from the hydroxide simply and cheaply.

9. Lesage and Co. patented, on Jan. 20th, 1877, the preparation of *sodium bicarbonate* and ammonium nitrate by passing CO_2 into a mixed solution of sodium nitrate and *ammonium carbonate.*

V. The Manufacture of Soda from Soda-felspar.

This has been attempted several times; for instance, on Dec. 16th, 1856, Newton patented (as a communication) the heating of felspar with lime and calcium phosphate, whereby caustic alkalies were to be formed.

The only proposals in this direction offering any prospect of success are those made by Ward and Wynants (patents of Dec. 30th, 1857, and June 2nd, 1864; comp. also Hofmann's 'Report by the Juries,' p. 51). Felspar, ground as finely as Portland cement, is mixed with a quantity of fluor spar equivalent to the alkali contained in it, or with cryolite, also with chalk and calcium hydrate; and the whole is exposed to the heat of a cement-kiln. The mass frits, but, owing to the lime, remains porous and easy to lixiviate with water: the alkali of the felspar (potash or soda) dissolves as caustic; and the residue may be utilized as cement. Hofmann (*l. c.*) reports the splendid success of this process in recovering the *whole* of the potash contained in the felspar; Dullo (Wagner's Jahresb. 1865, p. 291) contests both the possibility of this and of employing the residue as a cement. In any case the cost of the process of Ward and Wynants renders it quite inapplicable to soda-felspar, even if it could be applied to potash-felspar.

CHAPTER IV.

THE MANUFACTURE OF SODA BY THE LEBLANC PROCESS: RAW MATERIALS.

THE raw materials of the manufacture of soda by the process of Leblanc are *sulphate of soda* (in Lancashire called *saltcake*), *carbonate of lime*, and *coal*. The quality of all three materials is of great importance for the quantitative and qualitative result of the process.

The *sulphate* is employed directly, just as it comes from the calcining-furnace (roaster, drier). Its ordinary composition and the properties which it ought to have, as well as its chemical examination, have been already described (p. 11 *et seqq.*); here we shall only point out the following.

Even from the outward appearance of sulphate it is possible to get a good idea whether it is well adapted for alkali-making or not. It should be very porous and in the state of fine powder, or at least "spongy;" any lumps present must be quite easily crushed with a spade, and then fall to fine powder. Hard lumps nearly always contain a core of raw common salt, which is known at once by its colour and texture; on crushing, its coarsely crystalline form and grey colour present a strong contrast to the fine-grained yellowish or white sulphate. Since sulphate containing salt fluxes more easily than in the pure state, pieces entirely fluxed, even if inwardly white, are also suspicious: probably owing to their deficient porosity, they work very badly in the black-ash furnace. It goes without saying that the purer the sulphate the better it is, since impure sulphate requires exactly the same expenditure of labour, fuel, and wear and tear of apparatus, and yet furnishes less soda and of a lower quality. The sulphate employed in alkali-

works usually contains about 96, at best 97, per cent. real Na_2SO_4. But the chemical composition is not every thing; the physical properties of the sulphate are also of importance for the black-ash process. Hard, lumpy, or fluxed sulphate, even if containing 97 per cent. pure, will not yield any good black ash, until it has been finely ground, which is much too costly an operation with such a hard material.

Even sufficiently pure sulphate is deteriorated by roasting so far that the ferric sulphate (always present in it) has been converted into red ferric oxide; such sulphate (termed "foxy") never makes good soda, probably because it is also too hard-burnt and consequently does not react so well in the black-ash furnace. Good sulphate accordingly ought to show a little, but not above 1·5 or *at most* 2 per cent. free acid (as SO_3); for in this case it will not, as a rule, contain more than 0·5 or at most 1 per cent. NaCl. The "free acid" of sulphate (by which term, as we have seen, p. 14, every thing is understood which reacts on litmus paper, viz. bisulphate, pyrosulphate, ferric sulphate, &c.) in the black-ash furnace is most probably expelled by the heat there prevailing; or a small part of it may be retained by lime. Thus much is a matter of experience, that even sulphate containing 2 per cent. free acid makes a good black ash, almost entirely free from sulphate and sulphide (see also Davis, Chem. News, xxxii. p. 174). *Very* acid sulphate, of course, works badly, partly by forming calcium sulphate, which may remain undecomposed to some extent and afterwards on being lixiviated forms sodium sulphate again, and partly, in boiling-down pans heated from the top, by forming sulphate or chloride in the soda liquor by means of the acid vapours given off from the sulphate.

Sulphate, in the manufacture of which a great deal of nitrecake or, still worse, "cylinder-cake" (from making hydrochloric acid in cylinders) has been employed, does not easily yield good black ash, probably because such sulphate is rarely as uniform in its quality as that made from salt. But the author knows a few works turning out excellent alkali, although they use a very large quantity of nitre-cake in decomposing; but they always have the nitrecake ground before employing it.

It is an established experience that quite fresh sulphate, just as it comes out of the roaster, does not yield such good ash as that which has been lying for some time. Even outwardly the differ-

ence is noticeable: whilst fresh sulphate always shows more or less lumps and other irregularities in texture, that which has been lying for some time in a large heap looks quite regular and of even grain. In all probability, in such large heaps, which retain their heat for a long time, a further reaction takes place between the undecomposed sodium chloride and the excess acid, which improves the quality of the sulphate; the attraction of some moisture from the air, converting pyrosulphate ($Na_2S_2O_7$) into bisulphate ($NaHSO_4$), must exert a very favourable influence.

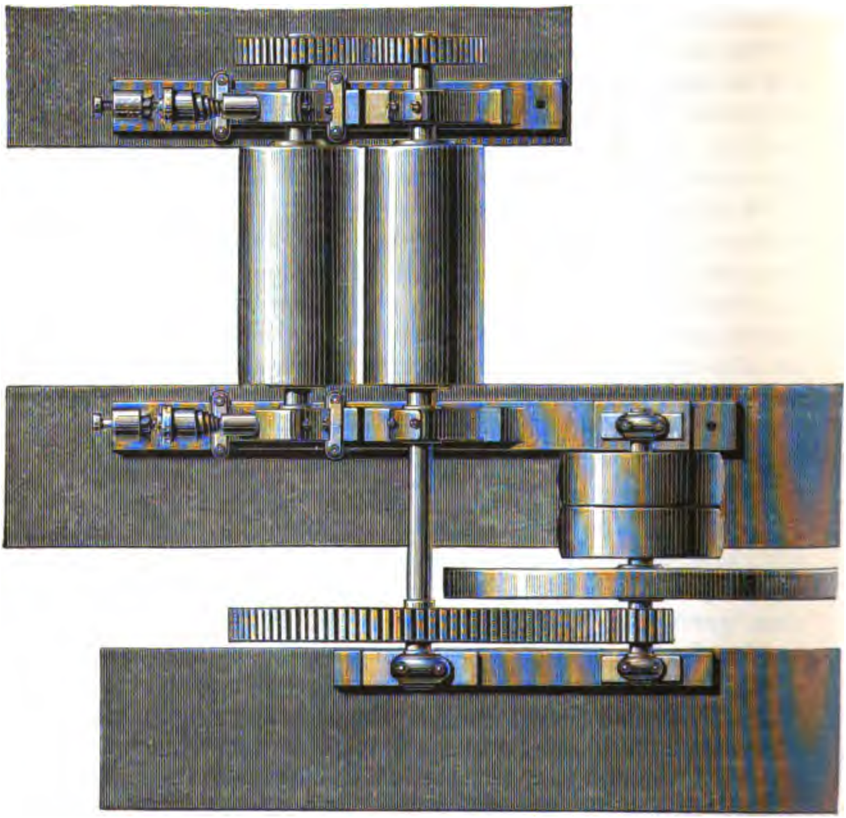
The statement found in some books, that frequently common salt is purposely left in sulphate, if weaker soda is aimed at, can only refer to the childhood and the crudest condition of alkali-making. Soda-ash is always made as strong as possible; if required weak, it is *afterwards* mixed with diluents.

As *calcium carbonate* both limestone and chalk are employed, and are, of course, all the better the purer they are. Sand, clay, iron, &c. contained in impure materials act prejudicially by forming double silicates with soda, which remain in the insoluble residue and cause a loss of soda. Large quantities of magnesia are also injurious; and dolomitic limestone is consequently not applicable. Quite innocuous are organic substances of a bituminous nature, which stain many limestones blue or even black; for these act in the black-ash furnace like coal.

Chalk is sometimes employed in pieces of the size of a fist, obtained by breaking by hand. All the better works, however, crush the chalk either by edge-runners or by rollers; for it is certain that unground chalk yields an ash one or two per cent. weaker than ground chalk. Only in revolving furnaces is block chalk employed, as we shall see. Fine grinding is not necessary; crushing to the size of a walnut down to that of fine powder will do. If the chalk is very damp, a quarter, one third, or sometimes half of it must be dried and mixed with the other in grinding; for otherwise the whole will be crushed into a tough paste, which is worse than unground chalk. The drying is done by waste heat or by some very cheap fuel, *e. g.* cinders picked out from the furnace-ashes. Any kind of furnace will do for drying; a good one is a deep furnace, in which the chalk is laid on a pigeon-holed arch, below which is the fireplace. The smoke either comes out at the top, or is taken away from there by a flue into the chimney.

Fig. 163 shows a convenient form of crushing-rollers for chalk; fig. 164 shows the "edge-runners" employed for the same purpose. When wet chalk is used, of course its varying moisture must be taken into account in making the soda-mixture. That used on the Tyne contains on the average 20 per cent. moisture;

Fig. 163.

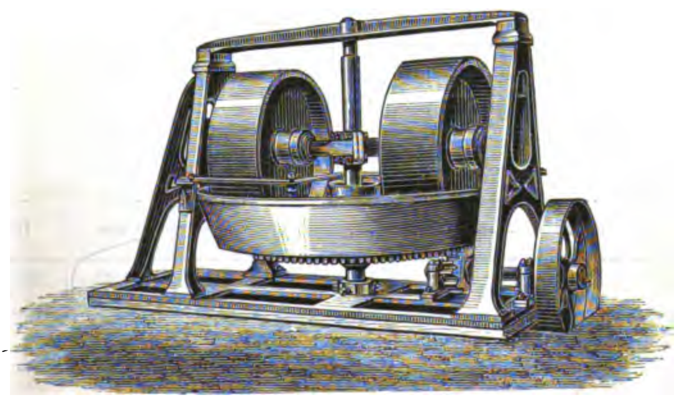


and the mixtures given below all refer to chalk in this state. Formerly all the Tyneside works used "London Chalk" from Greenhithe, Northfleet, and other places on the Thames, which the colliers took down with them as ballast, and delivered to the factory wharves at or even below cost price. "Block chalk" is

much purer than "cobbles" (*i. e.* pieces of the size of a walnut to that of an apple) or "small chalk;" the former is consequently always preferred. Recently the great extension of screw colliers, all using water ballast, has considerably raised the price of such chalk (formerly on the average 2*s.* or 2*s.* 6*d.* per ton); and several of the Tyneside works have been compelled to introduce limestone, dearer and worse though it be. The "French cliff" from the banks of the Seine below Rouen, also coming to the Tyne as ballast, has always been much too dear to serve for black-ash mixing, except in great emergencies; as it is harder than chalk, it must be finely ground first.

Where no chalk can be had, limestone is employed; this must

Fig. 164.



always be crushed to the size of a pea or a bean, by rollers, edge-runners, &c. In Lancashire the alkali-works buy the limestone ready crushed, delivered in trucks at their works, at about 6*s.* per ton. The best limestone comes frem Buxton, in Derbyshire, other descriptions from Cheshire, Wales, and Ireland. It might be supposed that limestone must be ground very fine to equal ground chalk in the furnace: but it is not so; for the roughly crushed limestone, universally employed in Lancashire, works much more easily in the furnace than London chalk; the balls in the former case are much more quickly finished than in the latter.

Formerly some works on the Continent are said to have burnt their limestone to lime and slaked this to powder before mixing;

this is probably nowhere done now. Freshwater or mountain limestones are said to be the best varieties for this purpose.

The following are analyses of limestone and chalk for alkali-works :—

	I. *Clapham.* London Chalk.	II. *Davis.* Buxton limestone.	III. Minera limestone.	IV. Ruthin limestone.
Calcium carbonate	78·000	99·372	98·298	98·370
Magnesium carbonate	trace	0·116	0·756	0·756
Ferric oxide (or ferrous carbonate)	0·200	0·187	0·348	0·252
Manganic oxide	0·150	0·013	0·022	0·026
Calcium sulphate	0·244	trace	trace	trace
„ phosphate	0·119	......	......	......
„ silicate	0·325	......	......	......
Sodium chloride	0·163	......	......	......
Alumina	0·220	0·123	0·145	0·135
Silica	0·600	0·106	0·442	0·398
Moisture	20·600	......	......	......
Organic substances	......	trace	trace	trace
	100·621	99·917	100·011	99·937

I. from Richardson and Watts's 'Chemical Technology,' iii. p. 235.
II. to IV. from Chem. News, xxxii. p. 175. These only refer to picked lumps; the average is much more impure.

We shall see afterwards that, besides limestone and chalk, also the *causticizing lime-mud* is employed for mixing.

At Aussig 15 per cent. of the limestone, which is somewhat dear there, is replaced by *desulphurized soda-waste,* the calcium sulphate of which does no harm, being converted into sulphide. Very much of this cannot be used, because the mixture becomes too bulky and the process irregular. We shall see, in Chapter XIV., that by the new process of Schaffner and Helbig the whole of the lime (or nearly so) would be recovered and used over again.

The quality of the *coals* employed for the black-ash mixture is also of very great importance. Which description of coal is most suitable is still a moot point, both in the books and among prac-

tical men. All, however, agree that good mixing-coal ought to contain as little ashes as possible; but some prefer bituminous, others more anthracite-like coal. In Hofmann's 'Report by the Juries,' p. 21, the former is demanded; but a few lines lower down the latter, with 80 per cent. coke and 4 to 9 per cent. of ash, is preferred to one yielding only 60 per cent. coke and 10 to 15 per cent. ash; and again a few lines lower down it is stated that in England the coal employed by alkali-manufacturers "generally" contains less than 5 per cent. of ashes. In reality many practical manufacturers believe that anthracite-like coal is less suitable for soda-making than bituminous coal; the more it cokes, the better it is; but, within the range of coking coals, of course those are best which yield the largest percentage of coke, apart from ashes, as the bituminous constituents are mostly driven out and burnt much too quickly to exercise much action in the furnace. Still they always act in penetrating the whole mixture and introducing the reduction, also in causing the coal to swell up and become porous, which is of use, since the mass in the furnace never gets melted into a real liquid, and the large surface of well-coking swelling-up coal will give better results than the small surface of a non-coking coal containing much more carbon. But, in direct opposition to these views, other, equally practised, manufacturers prefer a "dry" mixing coal to a bituminous one, because the batch in the former case does not heat so quickly, and the process then goes on more slowly and steadily, so that the men have proper time for working the ball through before it becomes too stiff and must be drawn out. These manufacturers try their mixing-coals in a platinum crucible, and prefer one coking very slowly and yielding a very high percentage of coke.

The latter certainly should not be caused by too high a percentage of *ash*. Coal-ashes, consisting principally of aluminium and calcium silicate and ferric oxide, cause the formation of sodium silicate. This, so far as it is dissolved, has about the same value as carbonate for most purposes, and in testing is always calculated as "available soda," as it is indicated by test acid along with carbonate and caustic. But at the same time, analogous to the manufacture of prussiate of potash, insoluble double silicates are always formed, which lock up a considerable portion of soda in a non-available form. With coal rich in ashes, consequently, much less and much weaker soda-ash is always obtained than with coal poor in ashes. This subject will have to occupy us again later on.

Frequently much stress is laid upon the freedom of mixing-coal from *iron sulphides* (pyrites). Practical men, however, agree that this constituent does little harm within moderate limits, such as those within which it usually occurs; up to 1·5 per cent. sulphur may occur even in very good mixing-coal.

Generally, it may be said that good mixing-coal contains little ash (less than 10 per cent.), cokes well, and yields much coke (65 to 73 per cent.). But it cannot be denied that the analysis and outward appearance of a coal do not give a certain clue to its suitability for mixing; some coals yield more and better soda-ash than others whose analytical data are much more favourable. When examining, not picked lumps, but samples of several cwt. reduced in the proper manner, the author has never met with an English mixing-coal containing less than 7 per cent. of ash. On the Rhine the alkali-works regularly employ washed "duff," containing only 5 per cent. ash. For a good mixing-coal a considerably higher price is paid than for a bad one, because the loss in quantity and strength of the ash is much greater than the difference in price of the coal. A contract for mixing-coal ought never to be entered into before making, in addition to the analysis, a prolonged trial of it on the large scale. The first black-ash balls will give an idea of the quality of the coal; but the yield of soda-ash can only be found out by a week's or a fortnight's trial.

Leblanc's original prescription was for charcoal. This, on account of its price, is hardly ever used now. Its porosity should be in its favour; but the author knows of a Hungarian alkali-works which was compelled to give up the use of wood-charcoal for soda-mixing, and to introduce real coal (much dearer there), because no proper black ash could be made with charcoal. Of course soda can be made by means of any other reducing body, such as coke, lignite, peat, sawdust, wood; but, for practical reasons, most of these cannot be employed, even if they are much cheaper than coal for equal reducing-value. Here, however, we must mention the experiments of Kolb (Ann. Chim. Phys. (4) vii. p. 218), which contradict the above-stated opinion, universally accepted in practice. Kolb concludes that coal acts not only by its carbon, or by the coke remaining on heating, but also by the hydrocarbons —that is, by its total reducing-property as it is indicated by Berthier's litharge assay, in which each 34·5 grams reduced lead represents 1 gram of pure carbon or its reducing equivalent of hydrogen (0·33 gram) or of hydrocarbons. [It is

well known, however, that Berthier's test is not only theoretically inexact, but, in the case of materials rich in hydrogen, illusory, because a portion of the hydrocarbons is always volatilized as such and escapes the oxidizing action of the litharge.]

Kolb operated on two mixtures, only differing from each other by their percentage of coal. In the first (J) it is supposed that the coal only acts by its carbon; in the second (M), that it acts by all its reducing elements, expressed in equivalents of coal. In spite of the difference in the quantity of coal, both mixtures yielded almost the same result; only the mixture J yielded a somewhat higher percentage of caustic in the ash. The mixture was made according to the formula

$$3\,Na_2SO_4 + 4\,CaCO_3 + 18\,C.$$

All the figures refer to kilograms.

Mixture J.

Sulphate	106	= 100	Na_2SO_4
Chalk	101	= 94	$CaCO_3$
Coal	75·5	= 50·7	carbon.

Result:—

Black ash of 39°	Decroiz	= 169·4
Soda ash of 90°	„	= 73·4

Mixture M.

Sulphate	106	= 100	Na_2SO_4
Chalk	101	= 94	$CaCO_3$
Coal	60·5	= 50·7	reducing elements, expressed in equivalents of C.

Result:—

Black ash of 41°	Decroiz	= 161·9
Soda ash of 89°	„	= 75·5

[These experiments of Kolb's have absolutely no practical value, because he employed *far too much coal* altogether; even his mixture M contains far more coal than ought to be employed; and it is no matter for surprise that the mixture J, containing a further excess of coal, could not furnish more ash than M.]

Kolb has further made experiments in which coal was replaced by other materials containing carbon, but according to another formula, viz.

$$3\,Na_2SO_4 + 4\,CaCO_3 + 13\,C.$$

The following mixture was always employed :—

100 Na_2SO_4 (*i. e.* 106 sulphate).
94 $CaCO_3$ (*i. e.* 101 chalk).
44 C (*i. e.* its equivalent of sundry combustible matters).

By representing the 44 carbon in this mixture by the following materials he obtained the results stated in the same lines with each, viz. :—

57·2	coke	yielded	163	black	ash	of 36° = 73·5	soda	ash	of	83°
70	charcoal	„	165	„	„	40° = 78	„	„		84°
301	sawdust	„	159	„	„	38° = 80	„	„		76°
56	coal-tar pitch	„	158	„	„	40° = 78	„	„		81°
166	peat	„	164	„	„	39° = 75	„	„		85°

It is perfectly true that these differences are not greater than those that obtain in working on the large scale with different batches made by the same mixing-coal; but still Kolb's conclusion, that it is indifferent which kind of coal or carboniferous substance is used (except coal containing pyrites), is quite unwarranted; and it is hardly possible to assume that any alkali-works' manager would actually make a mixture with sawdust or peat, instead of good coal. Kolb's experiments neglect, in the first place, the above-mentioned circumstance that Berthier's assay is not correct. Thus his 44 pure carbon are represented by the enormous quantity of 301 sawdust, which, for wood containing 20 per cent. moisture and in the dry state 50 per cent. C, 6 per cent. H, and 40 per cent. O, are theoretically equal to 127·5 carbon. In fact only that amount of the constituents of sawdust is available which would have remained behind on coking; and Kolb's own experiments thus entirely agree with the opinions stated above, but directly contradict his own conclusions. Secondly, Kolb says nothing about the fact, which he as a practical man must have known, that a mixture, either made exclusively with coke on the one hand, or with sawdust and peat on the other, could not be properly wrought in the furnace, and would yield abnormal black ash. The above results could only be

obtained by special experiments, made under his personal supervision and with particular care; and nothing is said about the cost of labour and fuel, or about the time required. This holds good even of different descriptions of coal, although they may have the same reducing action on lead.

Lignite (*Brown coal*) in some cases has been advantageously employed for soda-mixing; and there is no chemical reason why this should not be done, so long as the lignite fulfils the first condition of not containing too much ash. Earthy brown coal is not usable; but the so-called pitch-coal and other pure bituminous varieties are. A brown coal fit for gas-making, if poor in ashes, is also always fit for mixing. At Aussig the same Bohemian pitch-coal, containing 6 or 7 per cent. ash, is employed for making the gas for the works and the town, and for mixing; even the coke coming out of the gas-retorts, after being crushed, is employed in mixture along with fresh coal.

The *nitrogen* in coal, which varies from 0·5 to 1·75 per cent., mostly exerts an injurious action. If the mixing-coal contains much nitrogen, a strong smell of ammonia is noticed on drawing a ball, and also especially after standing some time in damp air. A large portion of the nitrogen, under the influence of the heat and the lime, will be converted in the furnace itself into ammonia, which, combined with the sulphurous and sulphuric acid of the gases, escapes in the form of white clouds from the chimney. Another portion of the nitrogen, under the influence of the alkalies and the carbon, is converted into sodium cyanide, of which part is converted into cyanate by the oxidizing action of the flame. It is the latter salt which continues the evolution of ammonia even after the balls are cooled down, since by the action of moisture the following reaction goes on:—

$$CONNa + 2\,H_2O = CO(OH)(ONa) + NH_3.$$

Sodium cyanate does not do much harm; but sodium cyanide, on the lixiviation of the black ash, must, exactly as in the manufacture of prussiate of potash, be converted into ferrocyanide by finely divided iron sulphide—nay, even by the iron of the vessels, which afterwards carries a very troublesome percentage of iron into the soda ash; on calcining, ferric oxide is formed, which discolours the ash. Where potash is made by Leblanc's process from potassium sulphate and coal containing much nitrogen, it pays to recover the

ferrocyanide arising in the above way; in the soda-manufacture this takes place quite exceptionally, as the solubilities of sodium ferrocyanide and carbonate do not favour their separation like those of the corresponding potassium salts*. Under similar circumstances mixing-coal containing but little nitrogen is more valuable than that which is rich in nitrogen; still better, but mostly too dear, are materials free from nitrogen, such as coal-tar pitch &c. It will be understood that in any case less sodium cyanide is found in "well fired" balls than in badly fired ones, just because in the former cyanate has been formed. Weldon (Chem. News, xxxviii. pp. 137 & 177) has proved by a number of data that the formation of cyanides (along with which sulphocyanides always appear) is observed to be more abundant at a lower temperature:—for instance, where wet causticizing mud is employed instead of limestone; in revolving furnaces generally, the charge in which is less hot than in hand-furnaces; but specially also where furnaces were working at a lower heat than usual; further, in the general English style of working, altogether different from the French style, the batches in the latter being left longer in the furnace &c.

A means of thoroughly getting rid of cyanogen compounds has been quite recently discovered by Pechiney, who adds, at the finish of an ordinary charge, some fresh sulphate, which destroys the cyanides and permits the liquors to be obtained free from iron; the details of this process will be found in the following chapters.

Analyses of good mixing-coals.

According to Richardson (Newcastle coal):—

Carbon	74·34
Hydrogen	4·96
Nitrogen	1·42
Oxygen	10·16
Sulphur	1·39
Ash	7·73
	100·00

* Weldon reports a case of a soda-works purposely increasing the cyanides in black ash by employing coal rich in nitrogen, in order to recover them; but it appears from the report that here also the quality of the ash fished from the liquors was unfavourable. (Chem. News, xxxviii. p. 177.)

According to Davis *l. c.* (Lancashire coal) :—

Combustible substance......	88·590	Carbon 70·122; Nitrogen 0·286
"Volatile" sulphur	1·387	Total ash 10·000; Total sulphur 1·432
Silica..........................	4·936	
Alumina	2·575	
Ferric oxide	1·511	
Lime	0·700	
Magnesia	0·052	
Sulphur trioxide	0·243	
Phosphorus pentoxide	0·006	
	100·000	

Pattinson (Trans. Newc. Chem. Soc. iv. p. 183) gives analyses of superior (1 to 6) and inferior (7 to 9) mixing-coal used at Tyneside alkali-works.

No.	Coke less ashes.	Bituminous substance.	Volatile sulphur.	Sulphur in ashes.	Total sulphur.	Ashes.	Moisture.
1.	61·19	27·35	1·47	0·18	1·65	8·32	1·67
2.	63·11	25·60	1·38	0·32	1·70	8·76	1·15
3.	64·09	25·90	1·06	0·22	1·28	7·94	1·01
4.	68·01	25·27	0·78	0·11	0·89	4·80	1·14
5.	66·51	25·83	0·69	0·15	0·84	5·90	1·07
6.	66·45	25·72	0·59	0·12	0·71	6·18	1·06
7.	58·51	25·88	1·65	0·30	1·95	12·56	1·39
8.	56·00	27·26	0·68	0·46	1·14	14·42	1·64
9.	58·80	26·20	0·76	0·52	1·28	12·88	1·36

[In the discussion following upon Pattinson's paper one of the largest alkali-makers present remarked that coals with only 4 or 5 per cent. ashes, like Nos. 4 and 5, in practice only occurred quite exceptionally.]

Analyses of ashes of mixing-coals (Davis).

	A.	B.
Silica	49·36	48·74
Alumina	26·86	22·79
Ferric oxide	14·00	18·76
Lime	7·07	5·43
Magnesia	0·48	0·99
Sulphur trioxide	1·12	2·74
Phosphorus pentoxide	0·11	0·05
	99·00	99·50

Where a good coal with little ashes cannot be got, washing will in many cases be advisable for removing slate, pyrites, &c., as is done on a very large scale in many places for making coke. This is generally done on the principle of the impact sieve, and at any rate more cheaply than in the way proposed by Hargreaves ('Mechanics' Magazine,' 1868, p. 125), viz. putting the coal in a solution of sodium sulphate or sulphide of such high specific gravity that the coal will float in it, while the heavy impurities will sink to the bottom.

Wherever possible, the coal employed is *small coal* (*slack*), which is much cheaper than rough coal, especially near the collieries, where the freight, the same for both descriptions, does not make the difference of price comparatively less, which the freight for longer distances certainly does. When a factory has to get its mixing-coal from a long distance, sometimes paying considerably more for freight than for the coal itself, it is often cheaper to get rough coal, because it contains less ashes than small. But then the coal must be crushed. In opposition to the opinion sometimes expressed, that a coarse grain of the mixing-coal is required for making porous balls, it should be stated, from practical experience, that, for equal quality as regards ashes and carbon &c., a coal works all the better the more finely it is divided; of a very small coal less will be required than of the same coal in pieces of the size of a walnut or an apple. The author knows of excellent results obtained with the finest dust or "duff." The porosity of black-ash ought not to be attained by pieces of coal remaining in it, but in a different way; moreover good mixing-coals mostly coke more or less; so that

the fine powder is agglomerated again, but in such a way as to enclose particles of sulphate and chalk and to act chemically upon them.

Where the coal is not employed in lumps (*i.e.* in the great majority of cases), it is rarely ground by itself, but only deprived of large pieces by passing it through a screen. The mixing-materials are usually not mixed with each other beforehand; but barrows containing each of them separately are tipped in front of the furnace, and they are only mixed by the operation of shovelling them into the furnace. It is best first to tip the chalk (or limestone), then the coals, last of all the sulphate. The latter is by far the most valuable of the materials; and less of it is lost in this way. Moreover, on shovelling it in, it thus gets to lie more on the furnace-bottom; and the chalk and coal on the top of it prevent it from being mechanically carried away by the draught. In larger works the charge, to save time and cooling of the furnace, is usually tipped in all at once through a hopper in the furnace-roof, which supposes a tramway running on the top of the furnaces; in this case the sulphate is tipped first into the hopper. The materials are then only raked through roughly, more in order to spread them more evenly in the furnace than to mix them; the latter takes place properly only later on.

It is, however, advisable not to be satisfied with this superficial kind of mixing; better crushing and mixing of the materials will be found to pay very well. This is done very easily by tipping them into a hopper below which a pair of fluted rollers (like those in fig. 163, p. 364) are fixed. In this case the chalk need not be separately ground, but may be put in in lumps, since it will be crushed with the other materials; and it is not even necessary to dry it, as its moisture will be absorbed by the sulphate and the whole will be easily crushed between the rollers. The weighed, mixed, and crushed materials for each batch may be tipped through a grating into waggons, which will take them straight to the charging-hoppers; if there is no natural difference of levels, the waggons must be lifted by hydraulic or other power; or else the crushed materials may fall through the grate into a small well and thence be taken up by an endless chain of buckets and tipped at the top into the hoppers.

For revolving black-ash furnaces the chalk need not be crushed at all; it is purposely employed in the damp state; and when it is

tipped into the white-hot furnace, the sudden evaporation of the water tears the pieces asunder with the force of an explosion, producing fine powder. But for these furnaces the coarse lumps or fluxings must be removed from the sulphate, either by passing it through crushing-rollers or through a screen on tipping it into the warehouse, and grinding the rough pieces by themselves; the sulphate from Jones's mechanical furnace is fine enough without this.

The proportions in which the materials are mixed vary much in different countries, and even in neighbouring works in the same country. A large proportion of the variations which appear in published statements or private notes are certainly owing to inequalities of the materials themselves; *e.g.* of chalk with 20 per cent. moisture much more is of course required than of dry limestone. When this is taken into account, it is found that on the whole the proportion between sodium sulphate and calcium carbonate does not differ very much; practice had long since discovered, what Scheurer-Kestner afterwards demonstrated, that no more of the latter should be employed than is required for complete decomposition. But the deviations in the proportion of coal are too great to be reduced to differences in the quality of the coal. French works usually employ much less mixing-coal than English ones; the German ones are about midway between.

Leblanc employed the following proportions:—

100 calcined sulphate,
100 chalk,
50 charcoal;

and, indeed, for hand furnaces the average mixture is still about the same as that indicated by Leblanc.

Kolb's mixture, *e. g.*, is

100 pure Na_2SO_4 (=106 commercial sulphate),
94 „ $CaCO_3$ (=101 chalk),
44 „ C (=52·5 bituminous coal).

Scheurer-Kestner (Rép. Chim. appl. 1862, p. 231) quotes the following mixtures of ten different works:—

	1.	2.	3.	4.	5.	6.	7.	8.	9.	10.
Sulphate.........	100	100	100	100	100	100	100	100	100	100
Chalk	107·7	110	103	97·5	115	121	115	93·6	100	90·2
Coal	73	50	61·7	55·6	35	46·6	68	40·4	40·3	42·1

Other published mixtures (all reduced to 100 sulphate) are the following:—

	1.	2.	3.	4.	5.	6.	7.
Sulphate..................	100	100	100	100	100	100	100
Chalk or limestone ...	115	121	115	100	97·5	107·7	100-108
Coal	30–35	46·6	68	75	55–59	73	66

	8.	9.	10.	11.	12.	13.	14.
Sulphate..................	100	100	100	100	100	100	100
Chalk or limestone ...	110–120	103	125	115	138	106	100
Coal	50	61·7	45	53	70	62·5	56·5–65

	15.	16.	17.
Sulphate..................	100	100	100
Chalk or limestone ...	117	110	107
Coal	64	60	40

Nos. 1, 2, 3 (from German works), Kerl-Stohmann, Techn. Chemie, v. p. 334; Nos. 4 and 5 (English works), *ib.*; Nos. 6 and 7, Muspratt; No. 8, Ure; No. 9, Brown; Nos. 10–15, from Richardson and Watts, vol. iii. p. 234 (viz. 10, a mixture of a French works for soda crystals; 11, the same for soap-making; 12, Lancashire mixing, with "slaked lime"; 13, the same, with quicklime [?]; 14 and 15, Tyneside mixtures); No. 16, Davis, Chem. News, xxxii. p. 176; No. 17, Fischer, Deutsch. chem. Ges. Ber. ix. p. 1559 (mixing-coal containing 9 per cent. ashes).

The author himself has observed the following mixtures:—

	1.	2.	3.	4.	5.	6.	7.
Sulphate..................	100	100	100	100	100	100	100
Chalk or limestone ...	112·5–120	105	95	104	220	103	100
Coal	46–52	53	56	60	67	60	45

	8.	9.	10.	11.
Sulphate..................	100	100	100	100
Chalk or limestone ...	100	100	104	101-2
Coal	32·7	34·8–36	36	39

No. 1. Own work, chalk varying according to moisture (10 to 20 per cent.), coal according to quality. 2. Mixture at St. Rollox in 1864 for soda ash. 3. Ditto for crystals, dry limestone. 4. Large Lancashire works, dry limestone. 5. Small works, employing caus-

ticizing mud with 50 per cent. water. 6. Large Tyneside works; dried chalk with 3 to 4 per cent. moisture. 7. Rhenish works (1878). 8. French works (1878); soda ash for bleachers. 9. The same, for ordinary ash. 10. French works (1878), making white caustic ash; sometimes for this purpose up to 110 chalk (dry) is taken, but for sulphate from rock-salt only 94 chalk. 11. Alsatian works.

All these are mixings for hand-furnaces; those for revolvers will be stated in that chapter. We would point out that, according to the theory of the soda-process later on represented by us as the most probable one, 5 molecules of sulphate, 7 of calcium carbonate, and 12 of carbon come into play—that is, 100 Na_2SO_4, 98·7 $CaCO_3$, and 20·3 C; of this, however, 2 molecules $CaCO_3$ and 2 molecules C are not required for the theoretical decomposition, but only for the practical operation, which demands the formation of a little CaO and CO at the close of the operation; without this only 70·4 $CaCO_3$ and 16·9 C would be required. Of carbon there is always much more needed, because a good deal of the coal simply burns in the furnace and another portion remains in the black ash. Of calcium carbonate the quantity first indicated cannot well be diminished for hand-furnaces; but we shall see that this is certainly done in revolving furnaces.

We shall lastly mention some mixings for the Pechiney-Weldon process which give excellent results:—

Sulphate	100·00	100·00
Limestone	79·40	75·00
Coal	41·60	38·20
Final sulphate	5·88	5·88
,, limestone dust	7·35	7·35

or on the whole,

Sulphate	100·00	100·00
Limestone	81·90	77·80
Coal	39·29	36·10

The most recent progress in soda-making has decisively shown that it is not only possible but advisable to cut down the quantity of calcium carbonate and coal in comparison with that of the sulphate, thus approximating it to the theoretical. For mechanical

reasons the latter will always have to be exceeded to some extent; but in Mactear's process (applicable to revolving furnaces) the quantity of limestone and lime has already been reduced to 80 per cent. of the sulphate. As to coal, the low percentage employed by the French works has recently been acknowledged on all sides to be the best possible for good *quality* of the ash. Even less than 30 per cent. is now sometimes used; but when the quantity is reduced so far, there is some danger of not decomposing all the sulphate and thus losing in yield. Equally low is the proportion of limestone in the Pechiney-Weldon process.

CHAPTER V.

THE BLACK-ASH FURNACES.

The black-ash mixture is always heated in a reverberatory furnace, which on the whole is of a very simple shape, with the exception of the mechanical or cylinder furnaces (to be described afterwards). Still a number of precautions must be observed in their construction, without which either the necessary heat will not be attained or the furnace will be worn out too quickly.

The furnace originally employed by Leblanc and Dizé was rectangular, and had a small working-bed along with a very large fireplace (6 ft. 6 in. × 2 ft.). J.-B. Payen, who first carried out Leblanc's process on a large scale, in 1796 improved the furnace by introducing a larger elliptical bed and a smaller fireplace (5 ft. 3 in. × 2 ft.). Further improvements were introduced in 1807 by Darcet and the Marseilles manufacturers; and ultimately Clément-Desormes constructed very large furnaces in order to save fuel and labour.

Payen gives the following table of the dimensions and production of these soda-furnaces (p. 381).

The last furnace constructed by Clément was thus four times as large as that of Payen; the charge worked from each of its four working-doors was as large as the total charge of one of the small furnaces. In the roof there were four charging-holes, usually closed. Payen also represents another furnace, employed in France and Germany until a recent period; fig. 165 gives a vertical longitudinal section, fig. 166 a plan, fig. 167 a cross section, on a scale of 1 to 100.

A is the fire-door; A′, the ash-pit; A″, the grate; B, the fire-bridge; C, interior of the furnace, the bed of which is dished about 5 inches deep; D D D are lateral working-doors; D′ D′, the same

	Length of bed.	Width of bed.	Surface of bed.	Charge. For 1 sq. met.	Charge. Total.	Number of batches per 24 hours.	Daily production.	Alkalimetral titre (Decroiz).
	metres.	metres.	sq. metres.	kilog.	kilog.		kilog.	
Rectangular furnace of Leblanc and Dizé......	2·00	1·40	2·80	40	112	6	672	26–30
Elliptical „ „ Payen	3·00	2·00	5·00	125	725	6	4340	32–35
„ „ „ Darcet	3·25	2·66	7·00	65	455	12	5244	33–36
„ „ „ Clément-Desormes	6·00	2·00	11·00	136	1496	6	8976	35–40
	9·00	3·00	24·00	136	3264	6	19584	

Fig. 165.

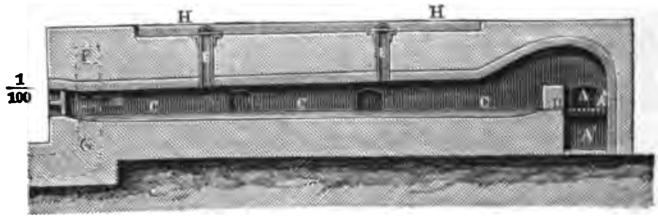


Fig. 166.

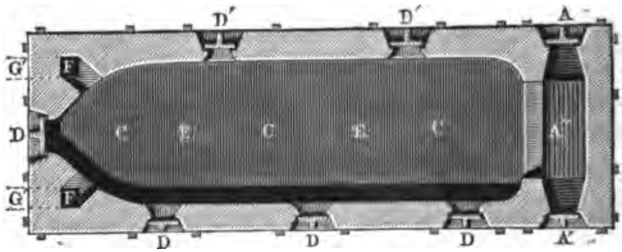


Fig. 167.

on the opposite side, for serving those parts of the furnace not reached by the tools from the other doors; E E, charging-holes in the roof, protected by cast-iron linings; F G, snore-holes for conveying the fire-gases into the flues G′ G′, through which the waste heat can be utilized for boiling-down pans &c.; H, the roof of the furnace, on which the mixture is spread and warmed for some hours previously to being tipped through the openings E E into the furnace.

Payen states the following details of work in these furnaces. On the average each charge consists of 935 kilog. sulphate, 986 chalk, 480 small coal, and 145 mother salts from refining. The fuel for 24 hours amounts to 2800 kilog. coal. The labour is done by 6

furnacemen and 6 assistants, who take their turns in three shifts of 8 hours each. 30 minutes are reckoned for charging and spreading the batch; 30, 35, and 20 minutes for the first, second, and third turning-over; 20 minutes for the last raking through and pulling out the batch. The whole labour takes 135 minutes; the pauses for resting between, 105 minutes; the total time for a batch, 240 minutes=4 hours. In 24 hours 6 batches of 1525 kilog. each, together 9150 kilog. of black ash are made, testing 38° Decroiz.

These large furnaces, which formerly were much more frequently found on the Continent than now, have considerable drawbacks, which have caused their almost total abolition in Germany, and their partial abandonment in France, in favour of the smaller English ball-furnaces. The only advantage attached to the large furnaces, a saving in fuel, is now attained with the smaller furnaces in a rational way by employing the waste heat for evaporating the lye, heating water, &c. In the large furnaces it is actually impossible to heat the bed any thing like uniformly all over; the batch will therefore in some places be finished and get burnt whilst in other places the reaction is still far behind. Nor can such very large charges be worked through evenly and ultimately fluxed to a homogeneous mass, at least not without heating them beyond their proper time. Certainly labour is not saved: 12 men in 24 hours get through 15276 kilog.=15 tons 5 cwt. of materials; whilst in a small English furnace with a 12 hours' shift two men manage 9 tons, with an 8 hours' shift three men 10 tons 2 cwt., in 24 hours.

Another description of furnace, figured in some treatises, hardly deserves to be mentioned, viz. that in which the flame of a small black-ash furnace travels over another dish-shaped furnace-bed, in which common salt is decomposed by sulphuric acid, so that all the hydrochloric acid escapes into the air along with the smoke! Such a barbarous apparatus is not imaginable in our times.

Kopp (Wurtz, Dictionn. ii. p. 1578) mentions a seemingly rational arrangement, in which the flame of the black-ash furnace heated a sulphate-furnace consisting of a pan and blind roaster; the flame first travelled round the muffle and at last underneath the pan. This plan has been given up again at the works where Kopp had found it, and that justly; for it belongs to the number of too finely drawn attempts at saving which in the end effect the contrary of the object they are intended to serve. Owing to the insufficient heat of the furnaces heated by the waste heat, the work

will take much more time than with direct firing; moreover one furnace perhaps requires a strong fire, whilst the other is not yet ready for it, and the first one must thus wait for the second; in short, ultimately for the same quantity of work turned out more time, labour, furnace-room, and mostly even more fuel are consumed than by other manufacturers who drive each apparatus by a separate fire, and consequently can force the work through. Of course these considerations are not intended to warn against utilizing the waste heat at all, but against irrational and exaggerated attempts at utilization.

According to Knapp (Chem. Technol. i. 2, p. 416), in Germany [formerly ?] furnaces with three oval beds occur, the lowest of which serves for finishing the charges, the two others, situated at a higher level alongside of each other, for a preliminary heating; the contents of these back beds are alternately pulled down into the working-bed. The furnaces combine a complicated construction with great liability to need repairs.

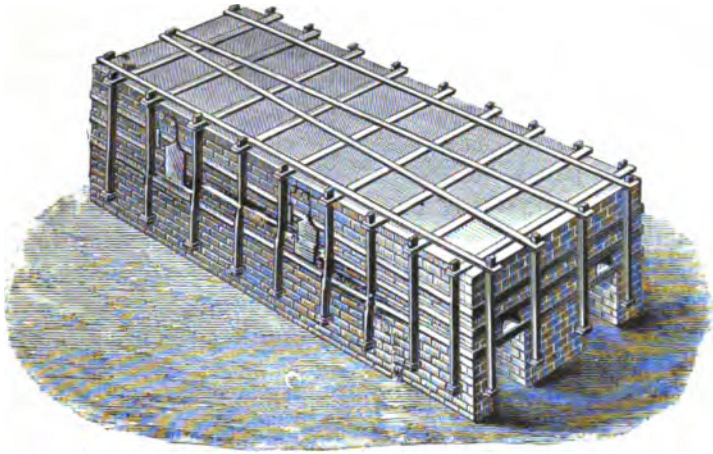
A furnace patented in 1868 by Perret is founded upon the same principle as his pyrites-burner (Vol. I. p. 193). It contains several shelves of fireclay slabs, through which the flame travels in a serpentine path from bottom to top; the heat given out by the mixing-coal assists the work. The lowest bed, which is fired directly, is only 4 ft. 7 in. wide. A practical application of this furnace is not probable; it cannot be expected to stand any length of time; and its object, better utilization of the heat, can be attained by employing the latter for evaporating the liquors.

In France, and also in Germany, sometimes large-bedded black-ash furnaces are found with one working-door on the same long side of the furnace as the fire-door, the other at right angles to it at the other end of the furnace, opposite the fire-door.

We will now describe the *English black-ash furnaces* (*ball-furnaces*), such as are now more and more found on the Continent as well. On the whole they are built on the same plan; they always have two (rarely three) beds, of which that more distant from the fire-bridge is a little higher than the front bed. The beds are comparatively very small, and only intended for a charge of 8 cwt., which is first put on the back bed, afterwards on the front or working-bed. Only quite exceptionally are larger charges worked in similar furnaces, *e.g.* 14 cwt. at Aussig.

The Lancashire furnace, of which fig. 168 gives a perspective

Fig. 168.



view, differs from the Tyneside furnace both in its larger size (it is from 8 to 12 inches wider and from 12 to 18 inches longer) and in its fireplaces. Instead of one large fireplace, with the grate-bars running from side to side of the furnace and charged from the front, the Lancashire furnace has two small fires, with bars running the long way of the furnace and charged from one end. They are also usually less substantially built than Tyneside furnaces. Even outwardly this difference is noted—that Tyneside furnaces are always cased in solid cast-iron front plates, whilst Lancashire furnaces are only bound by wrought-iron strips 3 to 6 inches broad and $\frac{3}{8}$ inch thick, about 6 inches apart from one another; these are pressed against the brickwork by the usual uprights and tie-rods. Sometimes even the working-doors are only protected by frames; but frequently metal plates are provided for these, reaching from the roof down to the bottom of the door, and held in their places by the two nearest uprights. The tie-rods of these are scarcely ever held on the uprights by screws and nuts, but by loops and wedges. Inside, the fire-bridges often have no bridge-plates and air-channels, which are never dispensed with on the Tyne. Sometimes in Lancashire there is fixed in the fire end of the furnaces, above the fire-doors, a cast-iron plate perforated by many holes, through which air is admitted into the furnace above the coals. This is intended to burn the smoke and save fuel, but often does the reverse; and consequently the holes are sometimes found plastered up again.

The construction of furnaces usual on the Tyne is shown in figs. 169 to 174 (working-drawings, of a very good furnace in actual work, all the dimensions being indicated in metrical measures). Here at the same time the boiling-down pan is shown, as it always accompanies the furnace.

Fig. 169 is a sectional plan along the line A B of fig. 170, passing through the hollow fire-bridge, but showing the beds and the pan from the top; fig. 170 is a sectional elevation along C D of the plan; fig. 172, one through the fire, along E F, looking towards the fire-bridge; fig. 173, one along G H, also looking towards the fire-bridge; fig. 174, a section through the pan, looking at the furnace; fig. 171, a front elevation, showing the firing-cave and the drainers in section.

Such a furnace serves for working 3-cwt. charges of sulphate along with the requisite quantity of chalk and coal; a "ball" is finished in 45 to 50 minutes (after having passed a similar time on the back bed); and, with the necessary pauses for cleaning the fire, changing shifts, &c., 24 to 27 balls are made daily.

a is the fireplace with its grates, consisting of wrought-iron bars, resting on three strong bearing-bars, set edgewise, so that there is not too much contact between them and the grate. Besides, a bar *b* is let into the brickwork lower down, to serve as a fulcrum for the large pokers with which the fire is broken up and cleared from below; *c* is a cave for facilitating the firing; this permits the ash-pit to be much lower than otherwise. Such a "cave-fire" consumes less fuel than an ordinary fireplace; perhaps, owing to the larger size of the ash-pit, the supply of air is more uniform; but probably it is more owing to the greater facility for minding the fire, so that not so much unburnt coal is raked through the bars. The fireplace must be lined with the best procurable firebricks, which must also be able to resist mechanical wear and tear by the tools. This holds good even more of the bricks composing the working-beds and the surrounding walls, but less of the arch. All of these must also resist the fluxing alkali for some time, of course only for a limited period. It is sufficient if the fireplace-lining lasts for three months, the working-bed five months, and the arch twelve months. The fireplace at the back, at *d*, is stepped backwards, so that the flame ranges all across the width of the furnace over the bridge *e*. The latter must be most carefully built; it is always very strong, 2 feet 6 inches to 3 feet 3 inches wide, and on the Tyne always *hollow*.

A cast-iron plate *f*, 1½ to 2 inches thick, reaches right across the bridge, half above and half below the level of the working-bed, and is protected by an air-channel *g* from burning or melting, on the side next to the fireplace. The air-channel is open at both ends; or if two furnaces are built back to back, it is provided with a small upright shaft to procure a constant draught in it. The object of the bridge-plate is principally to prevent fluxing of the black ash through the bed and the lower part of the bridge; this evil is much felt in Lancashire, where the plates are often wanting. Of course the air-channel must always be kept open: after some time it generally gets filled with fluxed black ash; and the fire-bridge must then be renewed. If this be neglected, the bridge-plate will get burnt, whilst otherwise it can serve many times over again.

h and *i* are the two furnace-beds. The charge is put through the hopper *k*, or, if none is provided, through the door, on the back bed *i*, which is 3 inches higher than the front bed; from this it passes onto the front or proper working-bed *h*, and is drawn out through its door. Three-bedded furnaces are but rarely met with. The beds are made in this way:—First the base of the furnace is walled up with common bricks to 12 inches below the level of the working-bed, or an 18-inch wall is made all round, the inner space filled up with broken bricks, and the whole paved on the top. Upon this foundation a firebrick wall, 9 inches thick, is made round the sides of the future beds and carried up to the abutment of the arch; this wall follows the outlines of the beds, and consequently has rounded corners at the back; in the front it slopes towards the two doors, between which there is a wedge-shaped centrepiece *l*. Now the site of the bed *h* is filled up 3 inches high with ground fireclay or ground chalk, and these are beaten down hard. Upon this the bed itself is made of bricks on end—that is, 9 inches deep; the bricks are set dry, as closely together as possible, and are driven in with the mallet, so as to leave the closest possible joints. The top is "grouted" with a thin paste of ground fireclay, in order to fill up the crevices between the stones. For the back bed, first three courses of common bricks are put on, some ground chalk is put on the top; and the bed itself is made of bricks on edge (*i. e.* 4½ inches deep), also wedged in as tightly as possible and grouted with fireclay. The drawing clearly indicates how the joints run, so that the tools shall meet with the smallest possible resistance.

The working-bed *h* slopes about 2 inches from the back to the

front door, in order to facilitate the working of the tools and especially the raking-out; the bed *i* requires very little or no slope. The back bed lasts a very long time, but the working-bed, at the best, four or five months; after this time it must be renewed, because too much stuff gets lost in it and because its inequalities do not allow the tools to work properly. Then the troublesome and expensive labour has to be undertaken of removing piecemeal the bricks of the bed, which are fluxed along with black ash into a very hard mass, and then putting in a new bed. In Lancashire, often only "false beds" are made; that is, the space hollowed out by wear and tear is filled up with fire-bricks whilst the furnace is at its highest heat, the bricks are levelled with a rake through the working-door as well as may be, a few shovelfuls of sulphate are thrown in, and these are fluxed down with closed doors. A false bed of this sort lasts one or two months.

Last of all the arch is made, 9 inches thick, for which specially shaped bricks have been placed previously as an abutment on the top course of the surrounding wall. In the arch a hole over the back bed *i* is left for putting in the hopper *k*, of sheet iron or very thin cast iron.

The furnaces on the Tyne are cased in solid cast-iron plates, 1 to 1½ inch thick, both back and front, and tied together by a number of uprights, made of strong railway-plates or oblong wrought-iron bars, 4×3 inches; at the bottom these are let into the ground 12 inches, and are there kept from turning over by stones of a foot cube; sometimes grooves are left in the foundation of the furnace for tie-rods, which are fastened like the upper ones. Above the furnace the uprights are always kept together by tie-rods of 1-inch round iron or ⅞-inch square iron, usually provided with a screw-thread on either end, which pass through holes in the uprights and are tightened up by nuts. The latter must be several times tightened up subsequently. In some places it is preferred to weld strong loops to the ends of the tie-rods which pass round the uprights; the tightening-up is done by driving iron wedges between the loop and the upright. This skeleton of casing and binders of course remains, even when the brickwork of the furnace is entirely worn out; the furnace-walls are consequently much thinner than is usual on the Continent, viz. 15 to at most 18 inches. This certainly causes rather more heat to be lost by radiation; but that is more than counterbalanced

by the longer duration of the furnace-lining, which does not become so hot; and the working of the furnace is easier if the front wall is thinner. The uprights are placed in such a way as to protect the parts suffering the greatest strain. The casing-plates are in one piece from top to bottom; but sideways of course the casing must be divided into several plates, whose joints are so arranged that they are always covered by an upright. Moreover they are connected inside by screwed-on patches or in some other way.

In order to facilitate the work, a small cast-iron plate is put in front of the working-door of *h*, where there is most wear and tear; there are also supporting-rods for the tools fixed in front of both doors, ending in loops which are put upon hooks bolted to the two nearest uprights.

The closing of the doors is best effected by means of fireclay slabs surrounded by an iron frame, and hung from cast-iron standards by means of a chain, pulley, and balance-weight. These are indicated in the elevation at one of the doors only; the cross sections show the doors (fig. 171) themselves.

Adjoining the furnace, but separated from it by a small air-channel *s*, is the *boiling-down pan*, *p*, which everywhere on the Tyne, and in many places elsewhere, is arranged for top heat. For hand-furnaces there is usually only one pan; but sometimes even here two pans are found side by side, as with revolving furnaces, each of which can be shut off from the draught by a damper during the cleaning-out. The pans are made of ⅜-inch sheet iron, riveted in such a way that the rivets and seams are as little as possible in the way of the tools for working the pan. For this purpose the plates run in whole lengths from back to front (towards the doors), without any cross seams.

The joints are either butt joints, with a strap at the bottom riveted to both plates, or, in the more usual construction of lap joints, the plates are laid so that the laps run on each side towards the doors; if, therefore, the rake is drawn towards a door, it slides from one plate to the other, and is not brought up by the seam. Sometimes the rivets are countersunk, especially in the "fishing pans" employed in Lancashire for bottom fire; for top-fired pans it is more usual simply to place the round rivet-heads on the top side and do the riveting on the bottom side.

The shape of the pan is so designed that its whole contents can be easily drawn out, as may be seen in the plan. Sometimes pans of that length are made with three doors; but usually they are made longer (a trifle above 20 feet for hand-furnaces), and then always with three doors, in order to better utilize the heat and to do more work. Round the top of the pans runs an angle-iron, turned inside, partly for stiffening it, and partly as an abutment for the arch. But as it is hardly strong enough for this purpose, frequently a special angle-bar *r* (figs. 171 & 174) is put on, which permits the arch to be made 9 inches thick instead of 4½ inches. In the corners, where the shape of the pan would cause an inconvenience, the wall is carried up to the top of the pan; the angle-bar is put on the top; and the arch is also sprung here of the same width as over the principal part of the pan.

Fig. 170 shows how the arch slopes down from the furnace towards the pan; sometimes the sides of the latter are shaped to suit this slope. This slope of the arch cannot be easily avoided, because on the one hand the pan-roof must be near the surface of the liquid so as to draw down the flame, for which reason the arch is sprung directly from one top edge of the pan to the other; but on the other hand there should be a sufficiently wide opening both for the flame to enter the space above the pan and for the fireclay slabs *o*, which form the bottom of the snore-hole and at the same time cover the air-channel *s* between furnace and pan, to project some way into the latter. This is done to protect the front end of the pan from burning and warping, to which it would be very much exposed if it were not cooled by the air-course and its top covered by the slabs *o*. Similar air-courses are left between the brick corners and the pan, sometimes even at the back end, although this is the coolest; the remainder of the pan-sides is in any case open to the air outside. In order to carry the slabs *o* more safely, sometimes a cast-iron saddle is put upon the pan-edge. The flue *t* is provided with a vertical or horizontal damper, and either leads directly into the main flue, or it is carried so as to make use of the remaining heat of the gases, which certainly must never interfere with the draught. This can be done in several ways; and we shall have more than one occasion to point out the waste heat of the black-ash furnaces as a source of heating other apparatus.

The pan rests upon pillars, *q q*, not quite going from side to side, so as to leave a free passage in the centre; they should leave the

seams accessible. Thus any leaks can be discovered and repaired by caulking without disturbing the working of the pan; moreover the pan-bottom is kept cooler in this way. It is well to cover the floor underneath the pan and the drainer with a layer of cement, and give this a little slope towards a catch-well in case of leakage. Such cases, however, ought not to occur at all if the pan is properly riveted and fixed.

In order to discharge the pan its front wall is interrupted in two or more places, and bent outwards for about 6 inches. The pan-bottom is continued into the necks formed in this way; the angle-iron connecting it with the pan-sides also turns round these corners, as seen in the plan fig. 169, whilst the upper angle-iron is interrupted in these places. Another angle-iron is riveted all round the openings formed in this way, as shown most clearly at *u'* in the elevation fig. 171. Against this leans the door *u* of ½-inch boiler-plate, without which the whole contents of the pan (which is sloped a little forward) would run out of the openings (door-frames). The doors are made fast in the following way:—The door-frame on each side has a slot (fig. 171, *u'*) through which bolts are put, each ending in front in a long loop. Through these loops a strong cross bar is put, strengthened in the centre and perforated by a screw-hole; through this passes a strong (2-inch) bolt upon which a corresponding worm is cut, and which in front is turned by a handle. Thus the door *u* is pressed against the frame; and lest it should suffer in the place where the bolt acts, it is strengthened there. It also carries one or two handles. The doors are not carried up to the full height of the pan; so that it is possible to work in the latter and observe its interior; in the meantime the loose cover *v'* (fig. 174) of sheet iron, with a handle, prevents the cold air from entering. Before putting on a door, its edge, where it will be in contact with the frame, is plastered with a thick paste of clay or lime-putty, most of which is forced out on turning the screw; the portion remaining in makes the joint good. Any small leakage does not much harm, as the liquor is caught in the drainer.

Figs. 175 to 177 show a somewhat different kind of door, which may be of cast iron; fig. 176 shows also a different mode of supporting the pan-arch.

In any case the arch must be bound by a skeleton of 2-inch

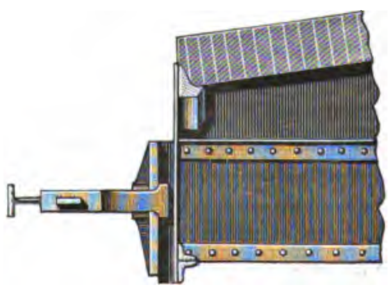
square uprights, kept together by tie-rods with screw ends both above and below the pan.

In front of the pan stands the *drainer, w,* made of $\frac{3}{16}$-inch iron, which is seen in fig. 170 from above, in fig. 174 in cross section, and in fig. 171 in longitudinal section. It has a perforated false bottom, *x*, consisting of plates 2 feet square, with holes $\frac{1}{8}$ to $\frac{1}{4}$ inch wide, resting on a framework of angle- and T-bars. The true bottom of the drainer slopes to one side, and ends in a well *w*, in which the liquor-pump *y* stands. The latter is shown on a larger scale by fig. 178. It is made entirely of iron, cast and wrought;

Fig. 175.

Fig. 177.

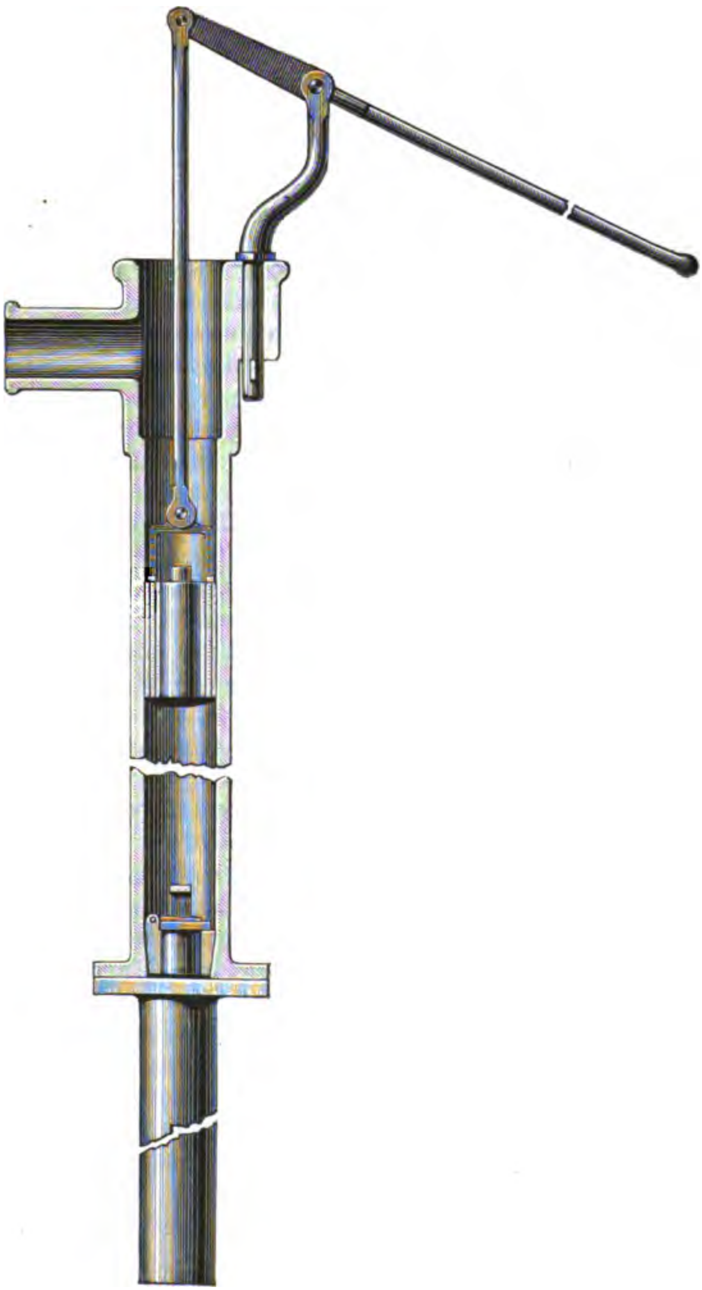
Fig. 176.



the clacks are ground to their seats; and the turned piston travels tightly in the bored-out barrel, since neither leather, nor hemp, nor oil is applicable for the caustic mother liquor. The pump is here drawn only high enough for pumping back the mother liquor into the pan; it may of course be made higher, if necessary, in order to keep the mother liquor by itself.

The work in the black-ash furnace is carried on in the following

Fig. 178.



manner:—The mixture is always first put on the back bed and levelled to some extent; during its stay there it is twice turned over with the paddle and a small rake, so as to expose fresh portions to the action of the fire. Here it is only thoroughly dried and heated; but it would be difficult to work it through properly, nor would this do much good, since the materials only begin to react upon one another when one of them has begun to flux. The mixture remains on the back bed till the working-bed, upon which in the meantime the preceding charge has been finished, is ready to receive it. This is not the case immediately after the preceding ball has been drawn; but the fire is allowed for some time to heat the empty furnace very thoroughly; then only the charge is pushed over from the back bed, through its working-door, by means of the paddle and rake. Often this is not done all at once, but about one third of the charge is left behind till the other two thirds have become very hot and are partially fluxed; then the last third is pushed over. In this way the mixture can be better turned over and overheating of portions of it avoided. On the Tyne this style of working (there called "splitting a ball") is quite usual. At the first pause after the back bed is empty, it is charged with a fresh batch, either from above by the hopper, or, in the absence of this, from the side through the door. In the latter case much cold air enters the furnace during the charging, and cools it down to some extent. If there are two back beds, the charge on the middle bed is first moved onto the front bed, then that on the back bed onto the middle bed.

The principal work of the ball-furnacemen takes place on the proper working-bed, the temperature of which gets up to a white heat; it is usually stated to be between the melting-heat of silver and that of copper. Ferd. Fischer (Deutsch. chem. Ges. Ber. ix. p. 1559) made exact observations of temperature by means of a Siemens electrical pyrometer, and found:—10 minutes after freshly charging, 713° C.; 30 minutes later, 779° C.; 15 minutes later, 874° C.; again 15 minutes later, just before drawing, 932° C. This refers to a furnace in which a charge of 3 cwt. sulphate is just finished in 1½ hour, whilst in England this only takes from 45 to 50 minutes; the temperature here must be accordingly higher. Kolb (*loc. cit.*) has made a series of experiments upon the temperature required for black-ash making, not by means of a pyrometer, like Fischer, but still sufficiently illustrating the influ-

ence of a rise of temperature; we shall report upon them later on, when describing the composition of ball soda, and will only remark here that Kolb considers a temperature near the melting-point of silver the most favourable one for soda-making. We shall also refer in that place to Hill's observations, according to which in the regular black-ash process the melting-heat of sodium sulphate is not attained.

Shortly after the mixture has been exposed to the intense heat of the working-bed, it alters its nature by softening at the surface. First of all the sulphate on the top, where it is touched by the flame, softens, and small clots are formed; so far as it is converted into sulphide, it fuses completely. Now begins the proper work of the furnaceman. He must with his tools (at this stage he works only with his "paddle" or "slice") turn over the mass so that no large lumps of sulphate, coke, &c. shall be formed, but the fused mass constantly brought into contact with unfused materials, especially sodium sulphide with calcium carbonate. Further, he must gradually raise all portions of the charge to the requisite temperature, which is done by moving with his paddle the upper portions towards the bottom and fetching up the portions lying first on the bed. The former, once soft, remain so on the bed as well, whilst the latter, now directly touched by the fire, attain the temperature required for their partial fusion.

During this work, of course the door must be open, which causes a large but unavoidable loss of heat; for this reason, though more especially because the labour is too heavy to be carried on uninterruptedly, the furnaceman only works a few minutes at a time in the furnace, and then leaves it about 10 minutes to itself with closed doors; it gets up its heat again during this interval. A second and third turnings-over with the paddle follow the first; during the two latter, if the ball has been "split," the remainder of the mixture is moved down.

In order to facilitate handling the large and heavy tools, there are always fixed in front of the working-doors either rollers or easily movable iron bars; the latter have three or four projections on the top, between which the shank of the tool is laid, and which serve as fulcra for its lever-like action. The men like to put some waggon-grease upon these bars, which makes the tools slide more easily upon them. The latter must be 5 feet longer than the width of the furnace, lest the men should have to approach too near.

Their weight is supported behind by a hook attached to a chain hanging down from the rafters; so that, while the man has principally to do the moving backwards and forwards of the tool and the turning-over of the stuff, the weight of the tool is almost entirely taken off him.

On the Tyne each ball-furnaceman has the following tools:—1st. A *paddle* (called *slice* in Lancashire) with a cast-iron head (fig. 180); the shank is 12 feet long exclusive of the handle; its

Fig. 179.

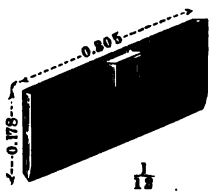
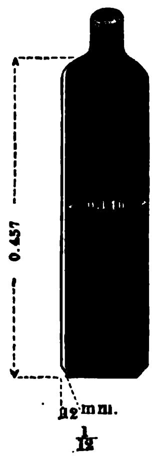


Fig. 180.



front part (next to the head) is, for the length of a yard, made of $1\frac{3}{8}$-inch, the remainder of $1\frac{1}{4}$-inch round iron. 2nd. Two paddles with wrought-iron heads, otherwise like No. 1: these are more easily handled, but do not last so long in the fluxed mixture. 3rd. A rake with cast-iron head (fig. 179), shank as above. 4th. A light rake with wrought-iron head of 11 inches width and 4 inches high; its shank is of only $\frac{3}{4}$-inch round iron. Besides, for firing, a rake with a shank 8 feet long and $\frac{3}{4}$ inch thick; a poker 9 feet long, 2 inches thick, flattened at the end like a crowbar, for breaking up the scars; a scar-hook with a shank like that of the rake; and a shovel.

The chemical action of the constituents of the soda mixture upon one another probably only begins after the mass has become partially fused. It never becomes a thin liquid, but always remains

pasty, principally because the lime does not fuse at all and the coal only cokes. There is consequently no danger of the charge running out at the door; at the worst a spadeful of ashes may be thrown onto the door-plate. About half an hour from beginning the labour on the working-bed the mass has become sufficiently liquid; and now the reaction must be carried through in as short a time as possible, by assiduous working. The furnaceman therefore exchanges the paddle for a rake (because now the mass does not offer so much resistance) and continuously turns the mass over, mixes it all, and gradually pulls it more and more towards the door. At this stage a large number of gas-bubbles (of carbon dioxide) escape from the mass, which sometimes presents the appearance of boiling. In the beginning no flame is seen arising from the mass; but gradually the latter, after being rather thin, becomes again more pasty or stiff, probably because the sodium sulphate has now been transformed into the less-fusible carbonate, and the gas-bubbles, which now also contain carbon monoxide, burst through with much more difficulty, owing to the toughness of the mass. This is the cause of continuous small jets of flame issuing from the places once opened by the rents in the surface of the batch—which are probably burning carbon monoxide, though coloured intensely yellow by the soda contained in the charge. We shall see later on, when speaking of the theory of the process, that carbon monoxide alone now appears, whilst the gas evolved previously was exclusively carbon dioxide, and thus could not produce a flame. These long pointed flames in Lancashire are known by the very appropriate name of "candles;" on the Tyne they are called "pipes." Their appearance in large numbers, combined with the fact of the mass getting stiffer, shows that the moment has come when the ball must be drawn out without any further delay. It would be quite wrong to wait till the appearance of the candles begins to *cease*, as some treatises direct. Scheurer-Kestner's explanation quite agrees with the opinion stated here (see Chapter VI.).

As during the last ten minutes the furnaceman cannot at all get away from the furnace, but must constantly work his rake in it, either he must previously run the bogie for receiving the ball to the furnace-door, and place it just underneath its ledge, or an assistant must do it for him. Usually the furnaceman has just before exchanged his hot rake for a cold one, and has greased both the shank of the latter and the bearing-rod; he now, whilst again

assiduously working the pasty mass through, pulls it into the bogie. If the operation has been a good one, if, therefore, the mass is stiff and not yet overheated, it will swell up greatly by the evolution of gas, similarly to a fermenting loaf of bread, and a large number of those pointed yellow flames will issue from it. If, according to the prescription given in some books, the drawing were delayed till the flame reaction is nearly finished, a burnt red ball would be got. On the contrary, if the ball has been fired too little, usually owing to insufficient heat in the furnace, it always remains too thin or "soft;" and this state is equally disadvantageous, because there is then much undecomposed sulphate in the mass. Pechiney has also pointed out that a high temperature at the finish yields much better ash in every way. The mass is stirred up even in the bogie with a small rake. At Aussig (where in 24 hours 23 balls of the unusually large size of 5 cwt. of sulphate are made) a portion of the process is purposely left to go on in the bogie, by not merely thoroughly stirring up the mass, but, according to its appearance, adding one or more spadefuls of coal and stirring it in. Everywhere else also a considerable portion of the reaction takes place in the bogies after drawing.

It goes without saying that the description here given does not exhaust the matter. The furnaceman must have a sort of intuitive judgment when a ball is finished; two or three minutes too much or too little can spoil it, as well as too much or too little fire, too much or too little draught; success consequently depends upon the experience, skill, and goodwill of the furnacemen. It is not at all indispensable to have many years' experience; the author has met with instances in which a furnaceman of 15 or 20 years' standing drew much worse balls than an intelligent, willing, and strong man who had only been placed as mixer or assistant with a furnaceman in order to learn the work. Working with chalk requires more heat than with limestone. Consequently men who are used to chalk, mostly "burn" their balls the first time on coming to a factory where limestone is used; in the opposite case they do not work hot enough, and get "soft" balls—that is, balls hard when cold, and not porous enough for lixiviation.

One of the most important matters in black-ash making is the assiduous and thorough turning-over of the mass,—first, in order to heat it uniformly; secondly, to mix the several parts as well as possible, to renew their points of contact, and to make the reaction

complete. That the results of the work are better with assiduous turning-over than otherwise, is not only a matter of course, but has also been proved by direct experiments made by Kolb (*l. c.*). With the same mixture of 106 sulphate (=100 Na_2SO_4), 101 chalk (=94 $CaCO_3$), and 53 coal (=44 C), he obtained the following results :—

A. Well-wrought ball.

162·2 parts black ash of 42°; 73·8 soda ash of 88° Decroiz.
Composition of soda ash—

$$\left.\begin{array}{r}62{\cdot}20\ Na_2CO_3\\ 4{\cdot}72\ Na_2O\end{array}\right\}=72{\cdot}2\ Na_2CO$$
$$\begin{array}{l}1{\cdot}12\ Na_2S\\ 2{\cdot}06\ Na_2SO_4\end{array}$$

B. Badly wrought ball.

160 parts of black ash of 42° Decroiz.
82 parts of soda ash of 82° Decroiz, consisting of

$$\left.\begin{array}{r}51{\cdot}20\ Na_2CO_3\\ 7{\cdot}15\ Na_2O\end{array}\right\}=63{\cdot}4\ Na_2CO_3$$
$$\begin{array}{l}4{\cdot}58\ Na_2S\\ 7{\cdot}48\ Na_2SO_4\end{array}$$

The turning-over of the mass has certainly some unavoidable drawbacks. During the time the doors are open much cold air gets into the furnace; the furnace-beds are very much worn out by the heavy tools; the labour is exceedingly heavy, and can only be done by very strong men and with restricted quantities. This makes the manufacture very dependent upon the ball-furnacemen, who in case of strikes cannot at once be replaced by fresh men. It is true that this labour is a purely mechanical one, and by men with sufficient bodily strength is easily learned, as we have said before; but just this suggests strongly the idea of replacing this expensive human labour altogether by cheaper and more reliable mechanical power. This has been realized, as we shall see, by the revolving ball-furnaces.

The furnacemen are not paid by the day, but by the number and quality of the balls drawn. As far as the latter is concerned, in most cases a deduction is made for bad balls; but in some instances

the payment is regulated directly by the alkalimetrical assay of the black ash.

Where larger batches than those containing 3 cwt. of sulphate are made, in the large French furnaces, several men must be put to one furnace. On p. 382 we have given the details, and seen that this arrangement differs, in every respect to its disadvantage, from the English work with small but frequent batches, even in regard to the consumption of fuel. Instead of 6 large charges, in England with two 12 hours' shifts 24 balls, with three 8 hours' shifts 27 balls are made in twenty-four hours. On the Tyne these are regularly made with 3 cwt. of sulphate, in Lancashire often with only 2½ cwt.; but then a few more of them are turned out.

Instances of the continental style of working are the following, seen by the author in 1878:—1st, 18 balls with 5 cwt. sulphate; 2nd, 24 balls with 3⅜ cwt.; 3rd, ? balls with 4 cwt. sulphate; 4th, 16 balls with 6½ cwt.; 5th, 10 balls with 10¾ cwt., of which half is drawn out at one time. In each case "per 24 hours" is understood.

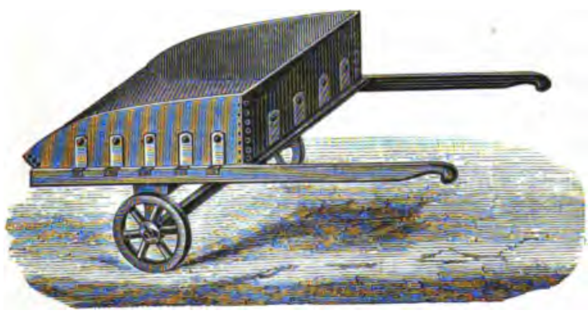
Several improvements have been proposed in the style of working the black-ash furnaces. The first of these was Leighton's patent of April 12th, 1836, for heating small coal and chalk in a furnace on a cast-iron pan lined with bricks, through which steam was introduced; upon this the sulphate was charged subsequently. Stevenson and Williamson's patent of Dec. 31st, 1855, also prescribes heating chalk and coal first, till some lime is formed, and introducing the sulphate with more coal afterwards. This process is not used in hand-furnaces; but it has been the means of making the introduction of revolving furnaces possible (see below). Gaskell's patent of April 12th, 1875, on the contrary, prescribes first charging the sulphate on the furnace-bed, and, when it has fluxed, adding chalk and coal. This proposal does not seem to be rational; it is not desirable for the process that the sulphate should be fluxed into lumps, as a good deal of it will thus be absorbed by the furnace-bottom. The processes of Mactear and of Pechiney-Weldon are intended for revolving furnaces, and will be described with these; but the latter process (adding some fresh sulphate and limestone dust at the finish, to destroy any cyanides and sulphides) is evidently also applicable for hand-furnaces.

The *draught* of black-ash furnaces must be carefully regulated. Before all things there must be *enough* draught—that is, a suffi-

ciently high and wide chimney and corresponding flues. This condition is not always fulfilled in smaller works; but its neglect is always revenged by a deficiency both in the quantity and the quality of the work turned out. On the other hand, too much draught is equally an evil; for the mass gets too hot, much coal is unnecessarily consumed, the black ash is easily "burnt," and much sulphate is mechanically carried away and lost. The furnacemen ought never to be allowed to alter the dampers of their own accord. Sometimes the working-door is connected with the (vertically placed) damper in such a way, by means of pulleys and chain, that on raising the former the latter goes down; this lessens the mechanical carrying away of sulphate and the rushing in of cold air during the turning over. But the radiant heat, so troublesome to the workmen, is even increased thereby.

The bogies serving for drawing the balls are shown in fig. 181.

Fig. 181.



They are made of $\frac{1}{4}$-inch boiler-plate; the sides of the box are joined to the higher end by angle-irons; the front consists of a little upbending of the bottom plate. This form of box, as shown by experience, is best adapted for loosening and tipping the solidified balls (by dropping the front end of the bogie, pushing the handles upwards, and thus allowing the contents to fall out); if needful, this is assisted by beating with an iron bar on the bottom. The bogies for 3-cwt. balls are 3 ft. long and 2 ft. 10 in. wide, at the back 1 ft. 1 in., and in front 3 inches deep. The bottom is joined to the sides by strips of iron riveted to the latter and passing through the former by means of a welded-on screw-thread, which is fastened below the bottom by a nut. The box thus formed rests

on a strong frame, with which the handles are made in one piece, of 2 × $\frac{3}{4}$-inch iron; this by vertical pieces is connected with a $1\frac{1}{2}$-inch axle, to which cast-iron wheels, 14 inches in diameter and $2\frac{1}{2}$ inches broad, are attached. The axle is nearer the higher (back) end; so that the bogie tilts over to the front, not to the back. The bogies are too heavy for pushing (like wheel-barrows); they are pulled by the furnaceman, whose labour is much lightened if the floor is covered with metal plates.

The balls are placed on edge with their thinner end downwards, the first against a wall, the following ones against the first; there should be room enough to store at least two (better three or more) days' work. They are tilted out of the bogies as soon as they have solidified, usually just before the bogie is required for drawing the next charge; so that they remain in it about three quarters of an hour.

The consumption of fuel for an ordinary black-ash furnace is very variously stated. With the wrought-iron grates usual in England, through which a great deal of unburnt coal and cinders is always lost, 13 cwt. of good firing-coals per ton of sulphate is a very fair figure; this includes boiling down all the liquor. If the English works had as rationally constructed fireplaces as the majority of the continental works, they would of course consume less coal than even these, looking at the better quality of their coal. Payen's 'Précis' (1877, i. p. 460) states the consumption of coal for hand-furnaces at 540 kilog., for revolvers at 370 kilog. per ton of black ash, which correspond to $17\frac{1}{4}$ and $11\frac{7}{8}$ cwt. respectively per ton of sulphate. The figure for hand-furnaces is evidently much too high. The same source (p. 453) states the consumption of coal in the large furnaces of Clément at 2800 kilog. for 6 batches of 935 kilog. of sulphate each, *i.e.* 50 per cent. of the sulphate; but this figure is hardly more reliable than the former. More trustworthy is the statement of F. Fischer (Deutsch. chem. Ges. Ber. ix. p. 1559), that in a Hanover alkali-works the firing-coal amounted to 64 kilog. for 100 sulphate, which entirely agrees with the author's statement respecting English works. But reliable notes taken by the author in 1878, both in Germany and France, show much better results. *E.g.* a Rhenish works burns 2 tons 4 cwt. of Saar coals for 18 balls of 5 cwt. of sulphate, including the evaporation of the liquor—that is, not quite 50 per cent. of the sulphate. Another Rhenish works burns 59 per cent. of the same coal. A third German works

burns 21 to 27, on the average 23 parts of Ruhr coal for 100 parts of black ash—that is, about 40 per cent. of the sulphate; the fireplace is a kind of gas-producer, which may lessen the mechanical loss by the grates. Statements obtained by the author from French works were:—1st. Upon 100 black ash *at most* 55 coal for firing and mixing together; this is 87 coal upon the sulphate, 32 to 35 of which are for mixing and the remainder for firing. 2nd. Upon 100 black ash 28 to 30 Saar coal for firing alone—that is, 42 to 45 upon 100 sulphate. 3rd. Indirectly, but very distinctly, 70 to 75 parts of coal for firing and mixing together were stated as the consumption of one of the best French works. We must not omit to notice that in some of these cases (*e. g.* that of 40 per cent. on the sulphate with a gas-producer) the heat remaining over did not suffice for boiling down all the liquor; but generally it does. Pechiney and Weldon have pointed out how irrational it is to make a fireplace of the furnace-bed, by using more mixing-coal than is necessary, merely for the purpose of boiling down the liquor, thereby running much more risk of burning the balls. It is far more rational to employ, in case of need, an additional fire for boiling down.

Revolving Black-ash Furnaces.

The fact that the labour of black-ash making (balling) is extremely arduous and that it is not always easy to procure the requisite number of skilled men, has naturally sometimes occasioned excessive demands for wages and sudden strikes. Yet the labour to be performed cannot be called "skilled" in the proper sense; all that is necessary is to turn over the materials thoroughly and to judge of the moment when this should cease and the ball be drawn out. It is evident that the former and much heavier part of the work, the turning-over of the mass, would be much better and more cheaply done by machinery than by manual labour; and the only question (certainly a very difficult one) is, how to construct a suitable apparatus for that purpose. The second point, judging the proper time for drawing the ball, does not require any strength, but an intelligent workman or foreman; and by the fact that machinery turns out much larger quantities at the same time than handwork, the recognition of the finishing point is made easier, and the number of operations is so much reduced that a single man can look after several furnaces, so far as this special point is concerned.

All this is so self-evident, that as soon as alkali-making had become a large trade in England endeavours to introduce machinery were made. Already on Jan. 27th, 1848, W. W. Pattinson patented a ball-furnace consisting of two circular beds, through the centres of which passed a cast-iron shaft, revolving in a footstep beneath. A circle of brickwork protected the shaft from coming into contact with the black-ash mixture. The shaft carried horizontal arms, to which a series of stirrers were attached. A stream of water flowed through the shaft and arms through a 1-inch pipe cast into them, for the purpose of preventing the iron from melting. The stirrers were very ingeniously arranged so as to turn over the mass as well as possible, and by reversing the motion could serve for discharging the mass. This principle agrees very nearly with that afterwards employed by Jones and Walsh for their mechanical furnace. Pattinson's furnace was tried on the large scale, but, owing to the rapid wear and tear, had to be abandoned again.

The successful principle, that of a cylindrical furnace revolving as a whole, was patented by Elliott and Russell on April 13th, 1853. This furnace was erected at St. Rollox soon after its invention; but it turned out to be too small and too badly constructed to compete with manual labour, then cheaper than at present. Moreover the black ash made in it was far too hard, and could not be properly lixiviated even by means of hot water. But Messrs. Stevenson and Williamson, of the Jarrow Chemical Works, South Shields, took up the project, and followed it out until, in the first place, they had improved the construction of the furnace in a number of details and brought down the wear and tear to a reasonable limit, and, secondly, had improved the style of working by the alteration already mentioned on p. 400, which gave the possibility of properly lixiviating the black ash. By first introducing the chalk and part of the coal and heating these for some time, till the chalk had been partly burnt to lime, and then adding the sulphate along with the remainder of the coal and finishing the operation, they attained the following results. The quicklime partly remained in the black ash, and was slaked when it came into contact with water, thus swelling-up and causing the hard mass to burst, so that the water could get into it and wash out the soda. (It is, however, certain that later on, when the temperature is lowered by introducing the sulphate, the largest portion of the quicklime at first formed is again con-

verted into calcium carbonate. Just for this reason Mactear's process, to be described below, is possibly more rational.)

The advantages claimed by Stevenson and Williamson for the cylinder furnace are as follows:—

1st. The continual motion of the furnace causes its contents to become heated with perfect uniformity, so that no part of the charge ever attains an excessive temperature; and thus the loss from volatilization is much diminished.

2nd. The mixing of the materials for the charge is effected without requiring the furnace to be opened for the introduction of implements, consequently without a current of air being drawn through the furnace during such mixing, thus providing for the atmosphere of the furnace being constantly devoid of free oxygen *.

3rd. From the much larger amount of work accomplished by the patent furnace at one time, a smaller number of skilled workmen is sufficient, the risk of bad work is diminished, and a more complete decomposition of the sulphate is ensured by the more perfect mixing.

4th. The waste of soda by absorption into the beds of the ordinary furnaces is avoided; and no tools being used in the process of mixing, the surface of the brick lining is less subject to injury from working than the bottoms of hand-furnaces.

Practice has shown that the better mixing indeed causes a more complete decomposition of the sulphate and yields stronger alkali. Whilst in hand-furnaces only exceptionally is 99 per cent. of the sulphate decomposed, this, and more than this, is constantly done in revolvers. But the mechanical properties of the black ash for a long time prevented the extension of the revolving ball-furnaces, and even led to the abandonment of some of those first erected. At first sufficient experience had not been gained to hit the proper moment for finishing; the balls were mostly overheated and bad to wash. The principal fault, however, was that the revolutions of the mass in the cylinder caused the gas to escape out of it too soon, so that the ball did not come out porous and honeycombed like hand-made balls. This made it difficult to wash completely, and

* In the experiments of F. Fischer (Deutsch. chem. Ges. Ber. ix. p. 1559), made with hand-furnaces, free oxygen was always found, even with closed doors usually 6 to 7 per cent., only once falling to 3·3 per cent. Of carbon monoxide only once a doubtful trace was found immediately after putting on a new fire, along with 7·6 per cent. oxygen.

caused a loss of soda. The indefatigable endeavours of Mr. J. C. Stevenson in the end overcame all difficulties, both of the mechanical construction and of the lixiviation of the balls. Whilst ten years ago the question was not altogether settled in favour of the cylinder furnaces, it has now been settled for some years.

It is certain that revolvers do not only better, but also cheaper work than hand-furnaces; and they are now introduced in all the larger alkali-works in Great Britain. On the Continent at present only a few of these furnaces have been built (at Lille, Rouen, Salindres, Mannheim, Hruschau). Most continental makers will not introduce them, because their erection is very expensive, the cheaper labour makes their advantage not so conspicuous as in England, and their very large turn-out (usually 12½ tons sulphate in 24 hours) makes them unsuitable for works of smaller dimensions. But even on the Continent the interest of the larger capital invested will be more than paid by the saving in labour; and the greater strength of the alkali remains as an advantage. It is true that there is no saving in fuel, if the steam required for the machinery is taken into account, except by Mactear's process, which labours under the disadvantage of producing a bad-coloured ash.

Leaving aside the older constructions of the revolving furnace, we shall only describe two of the most modern—viz. one with an ordinary fireplace, erected by Messrs. Carrick and Wardale of Gateshead for a whole series of alkali-works, and one with gaseous fuel, built by Messrs. R. Daglish and Co. at St. Helens.

The former furnace is shown in figs. 182 to 185. Fig. 182 is a sectional plan on the line CDEF of the next figure; fig. 183, a sectional elevation; fig. 184, a back elevation of the cylinder; fig. 185, a sectional elevation on the line AB of fig. 183. *a* is the fireplace, 5 ft. wide, 7 ft. long, and 7 ft. 6 in. high from the grate-bearers to the abutments of the roof. Owing to its large size, there are two fire-doors; the grate is worked only from below, an open space being left for this (fig. 183). Against the cylinder the fireplace has a circular opening of 2 ft. 9 in. width, through which the flame enters the furnace. First it passes through the "eye" *b* (that is, a cast-iron ring, strengthened by a rib, and hung by means of chain and pulleys). It has a diameter of 4 ft. 6 in., and is lined with fire-bricks so that a clear width of 2 ft. 9 in. remains. A similar opening, *d*, in the cylinder corresponds to the eye. On

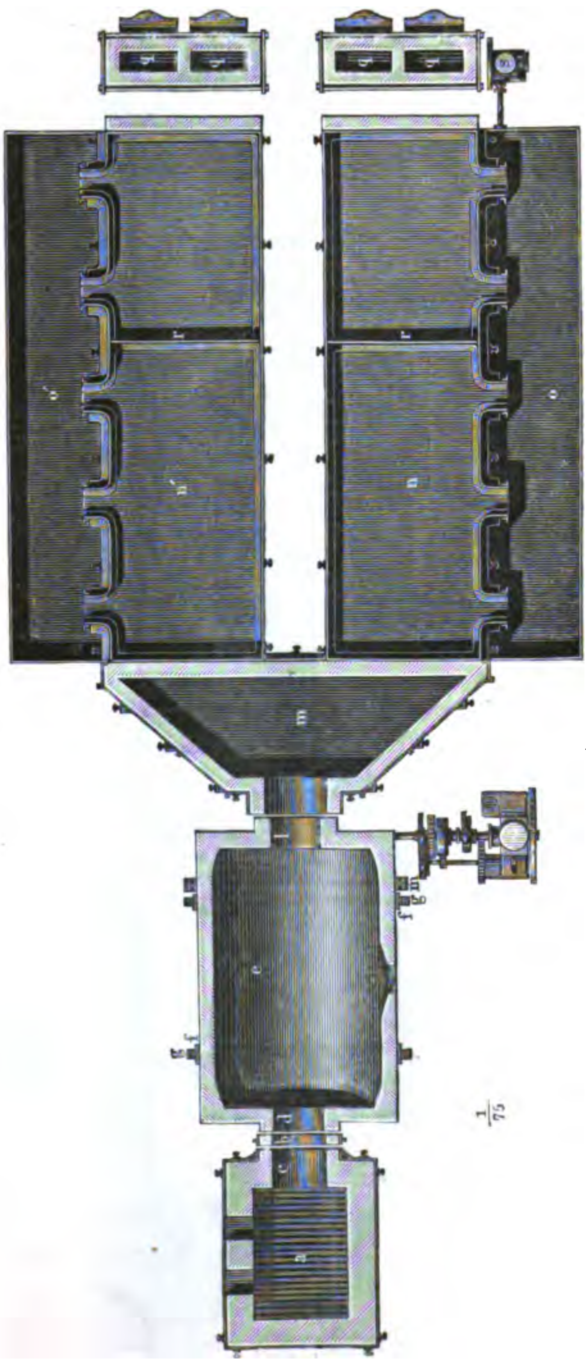


Fig. 182.

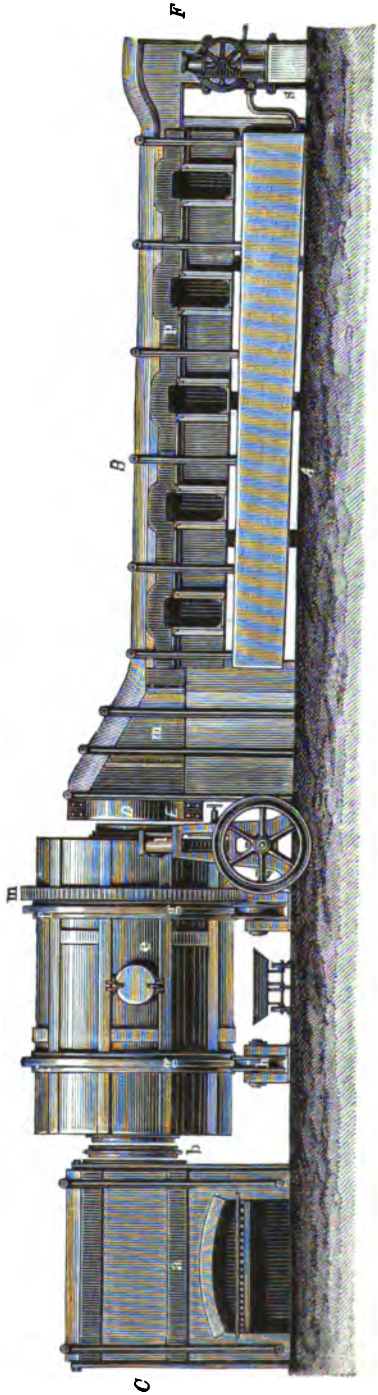


Fig. 183.

each side of the eye a space of 1 inch is left between it and the brickwork or the cylinder; on the cylinder side this is necessary to enable the same to revolve without communicating any jerkings

Fig. 184.

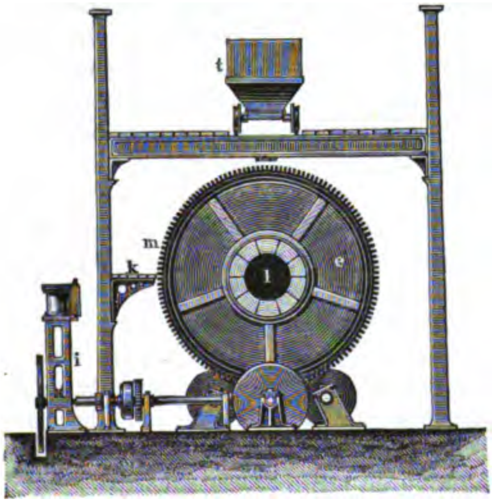
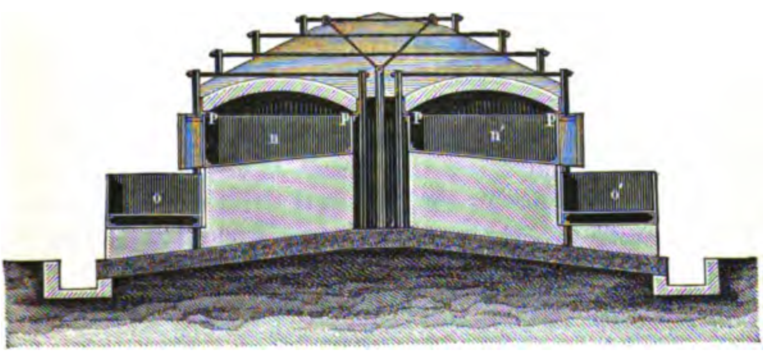


Fig. 185.



to the fireplace. Apart from this it has been found that such an air-space is necessary—probably because from such a deep fire much unburnt gas passes through *c*, which requires access of more

air for complete combustion. Moreover a certain amount of play is required, as the heat expands the cylinder. The cylinder *e* itself consists of a shell (barrel) of $\frac{1}{2}$-inch boiler-plate, 15 ft. 6 in. long and 10 ft. 2 in. in diameter inside. The seams are broken-jointed, butted, lapped at both sides, and double-riveted. The ends are specially strengthened by T-irons and gusset-plates. Upon the barrel strong cast-iron rings, *f f*, are fixed as tire-seats, truly bored and turned. The tires, *g g*, themselves are made of one piece of cast steel. They are carefully bored, and shrunk onto their seats, and bolted thereto with turned tapered bolts, and afterwards turned to work in the V rollers *h h*. The latter are specially shown in fig. 186 on a larger scale. They are made of cast steel, turned and bored, or of chilled cast iron. Their width between the flanges is 7 inches; and they are hollowed out in the centre to the depth of $\frac{1}{4}$ inch, so that in section they show the form of a very flat V (exaggerated in the figure). They are intended to secure that the cylinder shall run exactly on the friction-rollers *h h* without any side motion. Formerly, when the ordinary or somewhat more conical railway-tires were used, the furnace on revolving always moved a little from side to side till it was brought up by the flange, thus causing much inconvenience and damage. In Lancashire one of the rollers is made with a double flange, the other one quite plain, both of them with plane working surfaces; but here also the drawback avoided by the V rollers is experienced, that the furnace moves sideways till it is brought up by one of the flanges.

Fig. 186.

Formerly, as the tires made in one piece and shrunk on easily got loose by alternate contraction and expansion and thus sheared off the bolts, tires were sometimes made in segments with faced joints running diagonally; the bolts were countersunk and passed through an oblong hole in the cast-iron strengthening ring *f*; thus there could be expansion without shearing off the bolts. But this plan had also great drawbacks and was replaced by the cast-steel tires shrunk on in one piece.

The friction-rollers *h h* are, similarly to railway-wheels, bored out in the centre and fitted with forged $4\frac{1}{2}$-inch gudgeons, mounted on solid box-shaped double carriages, fitted with gun-metal bearings and bolted to the bed-plates. These plates, serving for the engine, carriages, and gearing, are of a strong box girder-form, all

strongly bolted together and secured to the foundations in such a manner as to form an entire unchangeable bed. The foundations consist of very large blocks of stone or, still better, of a single block of cement concrete. Sometimes in lieu of this a 2½-inch-thick bed of cast-iron is provided, made of several pieces kept together by a hoop shrunk on and fixed on the stone foundation by 1½-inch bolts.

The furnace is driven by a vertical engine with cylinder of 12¾ inches diameter and 14 inches stroke: it has double gearing; so that, by merely turning a lever, one revolution in four minutes or five revolutions per minute can be produced; another lever-handle gives instantaneous reversal of the motion. Usually the highest velocity does not exceed one revolution per minute. All the handles are within easy reach of a platform *k* (fig. 184), placed at the back end *l* of the furnace. The throwing in and out of gear is done by a large friction-clutch, worked by a hand-wheel and screw. Each furnace must have its own engine, because otherwise its motions will not be sufficiently under control.

The gearing acts upon a spur-wheel *m* laid round the barrel of the furnace and bolted to it immovably. (It is usually cast in one piece now.) The quick motion is obtained direct from the crank by a shaft bearing a worm which works in the spur-wheel; the slow motion is obtained by moving the friction-clutch so that the reducing gearing enters between the main shaft and the spur-wheel.

The cylinder is lined inside with the best fire-bricks; the lining in the centre is 9 inches, but at the ends 1 foot 6 inches; so that the interior of the furnace is barrel-shaped. This arrangement is made lest, on emptying, any part of the black ash should remain in the corners instead of running out of the man-hole. There are two horizontal rows of fireclay lumps in the lining, projecting 13 inches above the lining in the centre, 9 inches at the ends; these are called "breakers." The charge on revolving is constantly pushed against these breakers and thoroughly mixed thereby; and every part of it is exposed to the action of the fire, as the breakers drop it in the form of a cascade.

The man-hole has a diameter of 1 foot 6 inches, and is closed by an iron lid, which is sufficiently fastened by one or two wedges; these can be knocked off from the top when the furnace has to be

emptied; and the lid, previously hung by its handle with a chain, can then be lifted off.

Opposite to the entrance of the flame is the exit-opening *l*, of equal size with *d* (fig. 182). It communicates, but without an "eye," with the dust-chamber *m* (an apparatus which the strong draught of these furnaces renders indispensable), made wide enough to accommodate the two parallel boiling-down pans *n* and *n'*. The dust-chamber is about 6 feet long; its width next to the furnace is also 6 feet, that next to the pans 17 feet 6 inches (inside); its height is 11 feet at the furnace end and 7 feet 6 inches at the pan end. On the top it is covered by an arch sloping to the pans; its sides are kept together by a metal casing, binders, and tie-rods.

The *boiling-down pans* are each 28 feet long, 8 feet wide, and 2 feet 9 inches deep at the front side, 2 feet at the back side. Their bottom is therefore inclined forward, so as to get out the salt more easily. They have five working-doors each. The arch over them is carried by a special casting, *p p*. At the back end the fire goes through two flues, *g g*, with dampers, into the chimney. As these furnaces require much draught, each two of them have usually a chimney 6 feet in diameter and 100 feet high to themselves. Hill (Chem. News, xxx. p. 35) asserts that the temperature in the revolving furnaces is not so high as in hand-furnaces; but this can only refer to the temperature of the mass, not to that of the furnace itself.

Sometimes there is an open pan placed on the pan-arch for a first heating of the liquor, from which the proper pans *o o'* are fed.

Frequently the boiling-down pans are divided by a partition, *r*, into two unequal compartments—the larger one serving to evaporate fresh tank-liquor, the smaller one for the mother liquor pumped up from the drainer. By this division very strong ash (up to 57 per cent.) can be got out of the front drainer; the back drainer usually yields 50 to 52 per cent. ash. (Some of the most careful makers draw the *whole* of their ash from revolvers at 56 to 57 per cent. Na_2O, Liverpool test.)

In front of the pans are the *drainers, o o*, of the same length as the pans, 5 feet wide, 2 feet deep down to the perforated false bottom, and below this at one end 6 inches, at the other 14 inches deep; the space below is in communication with a steam-pump, *s*,

which pumps the liquor drained off back again into the boiling-down pan. If the latter is divided into two compartments, the drainers must be divided in like manner, so as to keep the strong and the weak salt apart.

Above the revolvers runs a *railway*, carried on bearers, which rest on brackets belonging to the pillars of the main building, as shown in fig. 184. On this the iron waggons *t* are run, which contain the charge and, through a temporarily put-on hopper, tip it into the man-hole of the cylinder. The waggons are generally charged by a special elevator, unless differences of level permit dispensing with this. In order to place all this apparatus, the building must be 30 feet high from the ground to the roof-frames.

A smaller railway runs underneath each cylinder, at right angles to its axis; on this stand the discharging "pots" in a continuous row, connected with each other by couplings; when the cylinder is emptying, they are filled one after the other, by slowly drawing them away from underneath the furnace by means of a chain passing round a capstan. These waggons or "pots" are built in such a way that their upper edges touch, as shown in figs. 187 and 188, lest any black ash should be lost between them. About twelve of these are required for each furnace. They are 3 ft. 3 in. broad and 2 ft. 3 in. long at the bottom, and 4 ft. 3 in. broad and 3 ft. 3 in. long at the top, and 9 in. deep; so that they yield a ball of this thickness.

A *revolving furnace heated by gas*, as erected by Messrs. R. Daglish & Co. at the British Alkali-works at Widnes, is shown in figs. 189 to 191. Here the cylinder has a diameter of 9 feet and a length of 16 feet. It is driven by an eight-horse-power engine, so that either one revolution in twenty minutes or in one minute can be made. It is heated by gas from a Siemens gas-producer. A A, the gas-flue; B B, the inlet-valve; C C, the combustion-space; D D, the inlet for previously-heated air; E, the expansion-ring (the "eye"); F F, the cylinder furnace itself; G, its manhole-door; I I, the friction-rollers; H H, the tires; J J, the foundation-girders seated on strong bed-plates K K; L L, the discharging-pots; M M, the steam-engine turning the cylinder and moving the pots L L (the latter is usually done by a hand-worked capstan); N N, the channel through which the air, heated by the waste fire of the

Fig. 187.

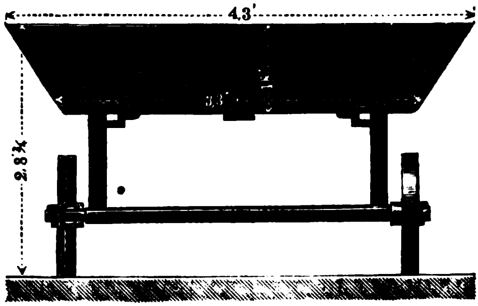


Fig. 188.

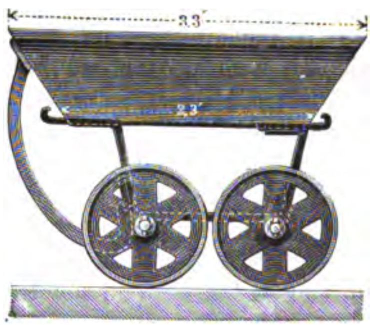


Fig. 189.

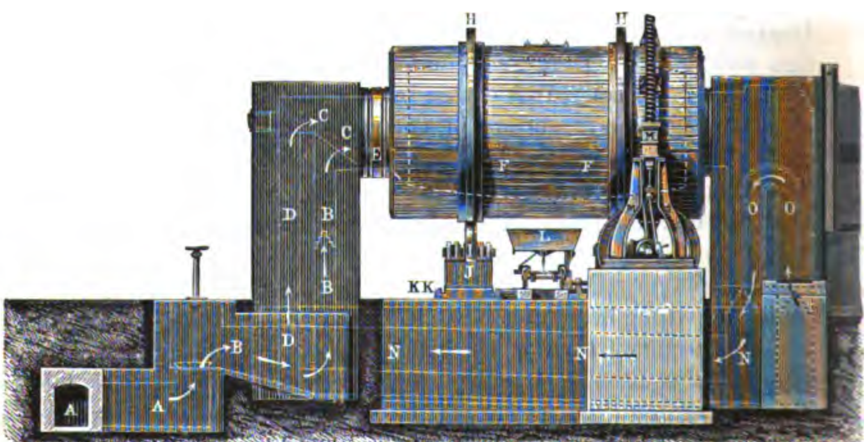


Fig. 190.

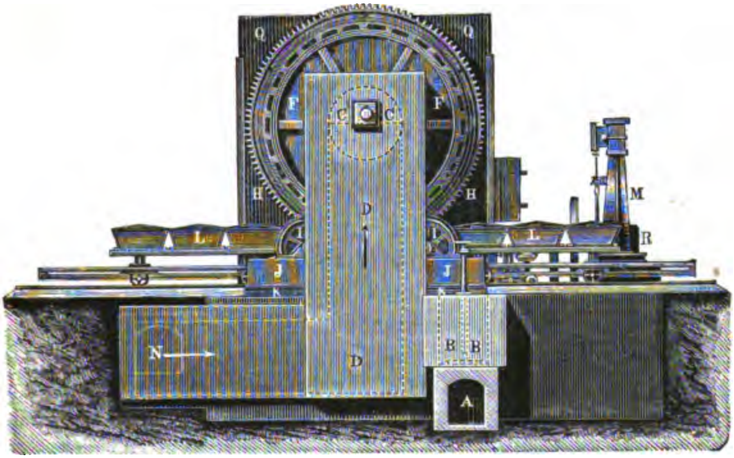
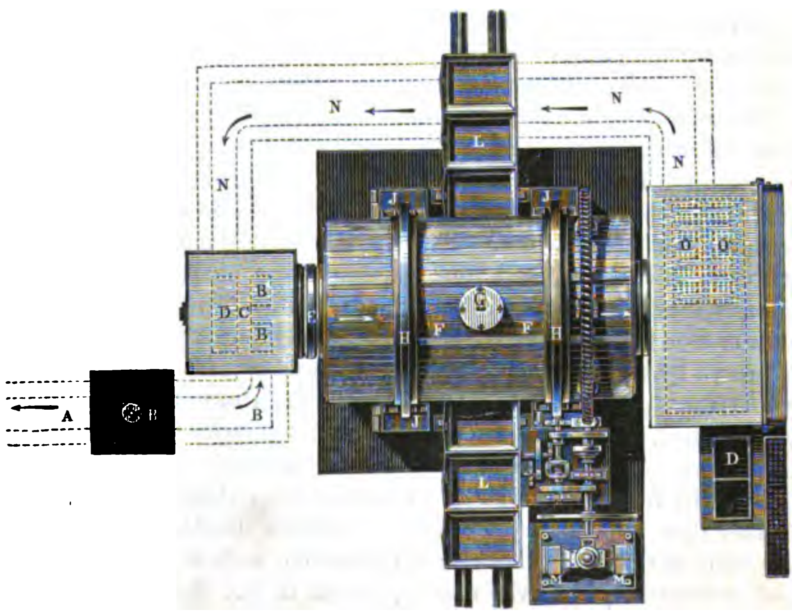


Fig. 191.



furnace, enters the combustion-space; O O, the cast-iron heating-apparatus for the same.

Heating by gas in the way sketched here has not been found economical, and has been abandoned; but this most certainly is not the fault of the principle of gas-heating, but that of the special arrangement. This is best proved by the fact that sometimes the necessary heat could not be obtained (Weldon, Chem. News, xxxviii. p. 137), which with a rational gas firing-apparatus most assuredly could not have happened.

Whilst the two descriptions of furnace according to the ordinary process only work up from 15 to 18 tons sulphate per 24 hours, Mactear has erected at St. Rollox and Hebburn much larger furnaces, by which, with the assistance of his new system of working, 50 tons of sulphate can be worked in 24 hours. In these furnaces the iron shell itself is built of a barrel-shape; so that the lining only follows its outlines. They are 18 feet 6 inches long, 12 feet 6 inches in diameter in the centre, 8 feet 6 inches at the ends; the fireplace is 18 feet long × 8 feet wide, and has three fire-doors. The boiling-down pan is 60 feet long. Each charge contains 4 tons of sulphate, and is finished in 2 hours.

A patent of Riley's (1878) introduces fireplaces at the two opposite ends; the exit is in the centre; and there is an arrangement for mechanically turning over the materials.

The method of working the revolvers, formerly universally, and now still usually employed, is the following. First all the chalk and two thirds of the coal are introduced, the chalk in lumps as it comes from the ships: the great heat to which they are exposed causes, within a few minutes, the moisture contained in them to evaporate with explosive force, and thus pulverizes the chalk much more cheaply than by grinding. The cylinder is then turned round with slow motion till a portion of the chalk has been burnt to lime, which is known by the appearance of a bluish flame of carbon monoxide round the man-hole, or at least by an admixture of blue in the yellow flame. The exact observation of this operation of "liming" is very essential, and requires some experience. Usually it is finished in from 1 to 1½ hour. This operation should not go any further than is necessary for getting sufficient quicklime to burst the balls in slaking; otherwise much caustic soda will be formed, and sodium sulphide will remain, which is not decomposed by caustic lime.

As soon as the proper point has been attained, the cylinder is placed with its man-hole upwards, and the sulphate (which must be of a fine grain and if necessary specially crushed to ensure this), along with the remainder of the coal, is dropped in. The slow rotation is still continued; and the damper is let down for about ten minutes, lest too much sulphate should be carried away. About 25 or 30 minutes after charging the sulphate, its fusion (?) is indicated by the appearance of a bright yellow flame round the working-door. Now the slow movement is at once changed into the quick one, and by means of a peep-hole in the pan-arch or the dust-chamber the process within the cylinder is observed, sometimes, to save the eyes, by means of blue glasses. It is noticed how the mass gradually becomes more and more glowing and passes from lumps into a pasty state; at last bright yellow flames break away from it, especially from those portions which hang on the breakers; this is a sign of finishing. The operation usually lasts with limestone 1¼ hour for liming and 1 hour for the work with the sulphate, together 2¼ hours; with chalk, 1½ hour for liming and ¾ to 1 hour for finishing, *i. e.* 2¼ to 2½ hours. In 24 hours ten batches are made. Newall (patent, Nov. 1st, 1877) heats the calcium carbonate in a separate furnace, but not up to the point of losing carbonic acid, and then charges the mixture all at once into the revolver —thus, like Mactear, dispensing with the "liming."

When the batch is finished, the furnace is turned round several times very quickly, so as to well agglomerate the mass and detach it from the sides; it is then placed with the man-hole upwards; the door is taken off, and the furnace slowly turned downwards, so that the black ash flows out and is taken up by the series of pots beneath, which are slowly drawn away. Mostly in this way nine pots are filled; then the furnace is once more turned round quickly, whereupon some more black ash is detached and fills another two or three pots. It shows in the pots, if properly made, exactly the same pointed flames, "candles" or "pipes," as hand-made ash, breaking forth in great numbers all over the surface of the ball.

The former charge of the furnaces at South Shields consisted of 26 cwt. chalk with 10½ cwt. coals, followed by 24 cwt. sulphate and 4½ cwt. coals, yielding daily from 18 to 19 tons of black ash. At Allhusen's the charge was 22 cwt. sulphate, 26½ cwt. chalk, and 12 cwt. coals; in full work 73 tons sulphate could be decomposed weekly; but, reckoning stoppages and repairs, only 66 tons, or the

work of three hand-furnaces, was actually made. The consumption of coals was the same for either kind of furnace, viz. 13 cwt. per ton of sulphate in the cylinder furnace inclusive of steam. With the latter the drying and grinding of chalk was saved, as well as 1*s*. per ton for labour. Cylinder soda was found not so well adapted for making crystals as hand-made soda, because it was too caustic. (This is contradicted by more recent experience; see below.)

The larger furnaces, like those described above, now decompose 30 cwt. of sulphate in each batch, or 15 tons daily, equal to the make of four hand-furnaces.

The mixture has also often been altered since Mactear showed that less limestone was necessary than was formerly assumed. At one large works now only 80 parts of chalk per cent. of sulphate is employed; but as no lime is added at the end (which would infringe Mactear's patent), much risk is run of either "burning" the black ash or not making it caustic enough to burst on lixiviation. At the Jarrow chemical works the mixture now (1878) is 100 sulphate, 90 chalk, 60 coals; here also the liquors are not found as free from sulphur as formerly. Of coal, for firing, 52 per cent. and, for steam, another 10 per cent. are consumed.

A revolving ball-furnace for 18 tons of sulphate per diem costs about £2000, inclusive of pans, pots, elevator, railway, &c., but exclusive of the building. It goes on an average four months before its lining must be renewed and it must be thoroughly overhauled, which takes a week. But the lining of the "eye" is very quickly burnt, and even with the best fire-bricks must be renewed every three, four, or five weeks, sometimes more frequently. There is therefore always a second eye lying ready on the furnace or hanging by a chain, which can be substituted for the worn-out one in a few minutes.

The liquors of properly made cylinder black ash are much less caustic than those from hand-made ash. Owing to this it mostly does not pay to work the mother liquors draining from the "black salt" for "cream caustic" (compare Chap. XIII.); but if caustic is to be made from them it has to be done by causticizing with lime.

Black and Hill (in their patent, 1874) attempted to modify the revolver process. Instead of "liming," they proposed to charge all the materials at once; and because the black ash thus made could not be lixiviated in the ordinary way, it was to be ground to

powder, put into vessels provided with mechanical agitators, and systematically washed with hot water, left to settle, and decanted. The advantages expected by the patentees were considerable; but as they have not been realized, and as this much more complicated system is nowhere carried out, we need not describe it in detail.

An important improvement was made in the working of revolving ball-furnaces by Mactear (patented Sept. 1874). The operation of "liming," necessary for the sake of lixiviating the balls, requires much more time than simple charging would, and also more fuel, capital, and labour. Moreover it is difficult to observe the proper point; and this can only be trusted to very experienced men. The idea of replacing this operation by adding some lime at the commencement had of course been carried out as well, but unsuccessfully. Mr. Mactear, starting at the other end, was more successful; and his process, worked since 1875 at St. Rollox, is now also in operation at some other works on the Tyne and in Lancashire. Mactear charges sulphate, coal, and limestone all together, but takes only as much of the latter as is required by theory; the operation is continued till the end of the decomposition is indicated by the fluid state of the mass. Now the cylinder is stopped for a moment, and ground quicklime to the amount of 6 to 10 per cent. on the weight of the sulphate, along with 14 to 16 per cent. cinders from the furnace-fires, are thrown in; the furnace is quickly turned round once or twice, to mix up the lime and cinders with the mass, which is then run out as usual. The addition of quicklime at the end of the operation gives all the advantages offered by the "liming" for the lixiviation of the mass; moreover the lime &c. cool the mass to some extent, and prevent it from being overheated during the last period. The cinders make the black ash more porous and easier to wash; they are also to save some mixing-coal. By adding more or less lime the soda can be made more or less caustic; this is very important, *e. g.*, for crystal-making. The advantages claimed by Mr. Mactear are as follows (but only the first four, according to very trustworthy information, can be considered really established by practical experience):—1st. As less calcium carbonate is employed, a good deal more sulphate can be decomposed in the same furnace. 2nd. As the liming is done away with, much time is saved, and consequently much more sulphate can be got through in the furnace. 3rd. Much limestone and coal are saved. 4th. There is 30 per cent. less tank-waste;

and consequently less insoluble soda is lost. [According to Mactear, 2½ per cent. of soda is to be gained by his process; but evidently this is greatly in excess of the truth. At any rate there is less expense for getting rid of the tank-waste; and its treatment for the recovery of sulphur is easier.] 5th. As the addition of quicklime is entirely under control, less caustic and sulphide are found in the liquors. [This is distinctly contradicted by most manufacturers; on the contrary, it seems established that Mactear black ash yields about 1 per cent. more sodium sulphide than ordinary cylinder black ash.] 6th. There is a higher yield of soda ash from the same weight of sulphate. [This would be the same as No. 4; but it is thus far a mere assertion, for which no data have been given.]

It must be said that some saving of soda ought to be expected, as in Scheurer-Kestner's experiments the insoluble soda in the tank-waste increased with the quantity of limestone in the mixture, which nobody had ventured to reduce as much as Mactear; but only experience can show whether such a saving actually takes place or not.

A drawback of Mactear's process, which is said to have caused some works to abandon it again, and which undoubtedly has prevented a number from introducing it, is this—that the soda ash made by it is inferior to ordinary revolver ash in strength and colour, owing to the larger percentage of sulphides in the liquors.

Mactear's mixture is 100 sulphate, 72 to 74 limestone, 40 coal, and at the finish 6 to 10 lime and 12 to 16 cinders. The lime can hardly play any chemical part, and only serves as a means for loosening the mass. When Mactear's mixture is compared with that usual since Leblanc (100 sulphate, 100 limestone, 50 to 60 coal), the large diminution in the amount of limestone and coal is at once apparent; and we shall see in the next chapter that the practical success of Mactear's process entirely explodes the old calcium-oxysulphide theory.

For firing, 50 parts coals, and 10 more for steam, per cent. of sulphate are required in Mactear's process. The wages are 1*s*. per ton of sulphate.

The work with Mactear's process must be very carefully superintended, so that the lime and cinders shall be put in at the exact moment when the process in the furnace is not quite finished; the temperature is then lowered, both by the cold materials put

in and by the immediate emptying of the mass; and as now the sodium carbonate is no longer protected by an excess of calcium carbonate, a backward reaction might set in. The reaction must be carried to completion in the pots, as with the hand-furnaces. Practically the style of work is this:—First the furnace is turned round slowly till the sulphate begins to fuse, then the quick motion follows till the yellow "candles" can be perceived through the peep-hole; now at once the lime and cinders are added; the furnace is turned round another five minutes, and then run out.

Whilst Mactear's process is only adapted for revolving furnaces, and moreover, according to general agreement, the drawback of a lower quality of alkali is connected with it, the process of Pechiney of Salindres (patented Dec. 24th, 1877, and Jan. 11th, 1878) seems to have got rid of that drawback, and especially if combined with the proposal of Weldon (patented Jan. 11th, 1878).

Pechiney observed that if fresh sulphate is added to a batch of black ash otherwise finished, quickly mixed with it, and the ball is drawn at once, the cyanogen compounds are all destroyed. (This explains why in the usual process such compounds are only found towards the end of the operation, when very little sulphate is left.) Consequently on lixiviation no sodium ferrocyanide can be formed by the iron sulphide always present—which, as is well known, cannot afterwards very well be removed from the liquors, is only destroyed on calcining, and discolours the soda ash by the ferric oxide which is formed from it. In this way perfectly white soda ash can be made without the process of refining, and that without keeping out any "red liquors." Even white soda crystals can be made direct from the tank-liquors. At the same time, as the sulphate ultimately added is also decomposed, the limestone and chalk of the mixture are much better utilized; and in this respect also most of the improvements claimed by Mactear are realized.

This process, however, is not complete without that patented by Weldon. In order to destroy the sodium sulphide which is otherwise always found in the tank-liquors, and more so in Mactear's process than in others, and which leads on the one hand to a loss of soda in the shape of regenerated sulphate, on the other hand to contamination with iron (as ferrosodium sulphide), Weldon adds at the last moment, along with the sulphate of Pechiney, some limestone-dust, which decomposes all the sodium sulphide present into carbonate; the tank-liquor thus becomes extraordinarily strong and

pure; and by directly boiling it down, without separating any mother liquors, white alkali of the quality of the soda made by the ammonia process is obtained. Of course the destruction of Na_2S by Weldon's process is not absolute; but it would appear to be sufficient for practical purposes. (We shall afterwards describe Pauli's process, which effects the destruction of sulphides even more completely.) The mixtures for the Pechiney-Weldon process have been already stated on p. 378.

The simplest explanation of Pechiney's process would be this :— The sodium cyanide reduces some sodium sulphate, forming cyanate and sulphide, thus—

$$Na_2SO_4 + 4NaCN = Na_2S + 4CONNa;$$

and the sulphide is converted into carbonate by means of the calcium carbonate still present or purposely added (according to Weldon), whilst the cyanate is no doubt destroyed in dissolving and boiling down the liquors, sodium carbonate and ammonia being formed. Weldon (Chem. News, xxxviii. p. 178), however, contests even the presence of cyanate in the black ash made by that process. According to him (as communicated to the author) the sulphate is reduced by the carbon of the cyanide; the latter is thus completely destroyed and cannot be brought back by any reducing agent. This might be represented by some such equation as

$$Na_2SO_4 + 2NaCN = Na_2S + Na_2CO_3 + CO + 2N.$$

Upon the merits of Pechiney's process there has been a discussion between Weldon and Mactear (Chem. News, xxxviii. pp. 130, 137, 162, 177; and a letter from Mr. Weldon, printed for private circulation), the more important points of which are as follows :—

Mactear contends that the formation of the cyanides can be prevented at the outset by working with a small proportion of mixing-coal (down to 29 per cent. of the sulphate) and, as in his patent process, with only 70 per cent. calcium carbonate. Thus the fusing-point of the mass is considerably lowered, and the decomposition of the sulphate takes place at a much lower temperature than usual; and this reduces the proportion of cyanide—which is principally formed at the end of the operation, when the temperature has risen very high.

To this Weldon replies that the opposite takes place, that more cyanides are formed at lower temperatures—of which he gives several instances. If in spite of this the cyanides are only found at the

end of the operation, when certainly the temperature is highest, this is caused by the fact that at that period the sulphate is almost entirely decomposed, whilst Pechiney has proved that in the presence of sulphates the cyanides cannot exist, or that they are destroyed by adding more sulphate. The latter is the only rational process, but, in order to make a good quality of alkali, is combined with a very high temperature and the lowest possible proportion of mixing-coal. This the French manufacturers, and especially Pechiney, have carried out long since, whilst Mactear has only recently experimented with a small proportion of mixing-coal, and employs too low a temperature.

Mactear contradicts all this. The cyanides are formed, not from the nitrogen of the mixing-coal, but by the action of atmospheric nitrogen on the alkalized carbon, which takes place only at very high temperatures. A very high temperature of the furnace, which he prefers himself, is compatible with a comparatively low temperature of the mass, which only depends upon its melting-point; and this is lower in his process than in the others, especially in the instances cited by Weldon. Other people had destroyed the cyanides before Pechiney; and they might be destroyed by his (Mactear's) process as well. It was also known before Pechiney that sulphate destroys the cyanides; the priority of employing a minimum quantity of mixing-coal did not belong, as far as Great Britain was concerned, to Pechiney, but to himself. Pechiney's white soda ash was probably made by a great excess of common salt in the liquors.

To this Weldon replies explicitly, showing, sentence by sentence, that Mactear had either misunderstood or misrepresented his statements, and that he had brought forward nothing essential in refutation of them. He proves that in reality the nitrogen of the mixing-coal, perhaps also the ammonia of the fire-gas, is the cause of the formation of cyanides. [With this entirely agrees an observation made by Dr. Pauli and communicated to the author, viz. that when, in the place of mixing-coal, coal-tar pitch is employed, which is free from nitrogen, black ash absolutely free from cyanides is obtained.] The best refutation of Mactear's position, according to which a lowering of the fusing-point of the mass lowers the proportion of cyanides, is that notoriously the soda-ash made by Mactear's process is of inferior colour. It is true that before Pechiney others had attempted to destroy the cyanides;

but Pechiney was the first to do this successfully on a manufacturing scale and in the simplest manner. That Pechiney's white soda, which rivals ammonia-soda in colour and strength, is most decidedly not produced by an excess of sodium chloride in the liquors, is proved by a long array of figures.

Several objections have been made to the Pechiney-Weldon process, which are discussed by the author in 'Dingler's Journal,' ccxxxii. p. 529, on the basis of communications received from various quarters and from Mr. Weldon himself. It was contended that, at least in one case, the great improvement which followed upon the introduction of that process was partly produced by substituting, at the same time, fishing-pans for pans heated by top fire. It was, however, distinctly proved to the author that this assertion is erroneous, no alteration whatever having taken place at that works in respect of the evaporating-pans, which had always been fishing-pans. It was further asserted that, owing to incomplete decomposition of the final sulphate, the alkali cannot be brought up to 58°, but only to 56° (Liverpool test). This is also emphatically contradicted by some who are working with the P.-W. process, who obtain regularly 58-per-cent. alkali, even with top heat. Again, it has been said that, owing to the small proportion of mixing-coal, there is not enough heat for boiling down all the liquors by the waste heat of the ball-furnace. But some manufacturers do this all the same; the others must either employ more mixing-coal, or, much better, assist the evaporation by a special fire, where the excess of coal is burnt for this purpose. It is true that the P.-W. process takes about 10 per cent. more time than the Mactear process; but this is no serious drawback. A more serious objection is this—that the P.-W. process causes a deficiency of yield of soda, either because much is lost by volatilization in the great heat, or because the black ash runs out too thin and turns too hard for perfect lixiviation. But at those works where the yield has been actually ascertained it has been found not less, but even larger, with the P.-W. process than with the old process. The black ash certainly comes out very thin; but it swells in the bogies to an unprecedented extent, so that for the same proportion of sulphate more bogie-space is required in the proportion of 14 to 11; the black ash is consequently extremely porous and very easily lixiviated.

It is true that the Pechiney-Weldon process is not so simple

as it looks. Each revolver must be studied by itself; and when to make the addition of final sulphate, what speed to use before and after that addition, how long time to run it afterwards, &c., must be found out by a series of trials. Owing to this the process can be only gradually introduced; but in May 1879 there were already sixteen revolvers running with this process, producing 2500 tons of soda ash per week, and a large number of British alkali-manufacturers were waiting their turn for the introduction of the process. Bad results, announced from some quarters where the process had been tried without the knowledge and assistance of the inventors, are no disproof of its value. In the very best cases the ferrocyanide in the liquors only amounts to 0·03 per cent. of the total alkali; but sometimes it rises to 0·29 per cent. In the liquors made by Mactear's process 1·0 to 1·06 of ferrocyanide per cent. of the total alkali is present (according to Weldon).

Since the Pechiney process forcibly drew the attention of all alkali-makers to the cyanides in black ash, a series of patents have been taken out for the same purpose, none of which, however, has hitherto entered into serious competition with that process. They are as follows:—

Mactear (No. 3079, Aug. 3, 1878) adds to the charge in the black-ash furnace, shortly before withdrawing it, certain "oxidizing" substances, viz. the sulphates of calcium, barium, or strontium, or the oxides of iron or manganese. When calcium sulphate is employed, 5 per cent. of the sodium sulphate suffices for destroying the cyanides.

According to Gaskell (Patent No. 3783, Sept. 25, 1878) the formation of cyanides may be prevented or diminished by blowing a current of air and steam upon the mass contained in the revolver during the whole operation, by means of an injector. In this way the carbon monoxide contained in the fire-gases is burnt into dioxide, which at the same time causes a saving of fuel. It is here assumed that the formation of cyanides is merely owing to the prevalence in the revolver-air of a reducing flame containing very much carbon monoxide; the current of air burns both this and the cyanide. The success of this process is as yet doubtful. It is moreover strange that there should be such a great difference between the atmosphere of revolvers and that of hand-wrought furnaces, whose gases contain a large proportion of oxygen and no carbon monoxide (F. Fischer, Berichte deutsch. chem. Ges. 1876,

p. 1558). Moreover, the Pechiney process is just as efficient in the latter, and was, indeed, fully worked out in hand-furnaces before it was tried in revolvers.

Brunner (No. 3166, Aug. 10, 1878) fluxes the sulphate and limestone first with a portion (25 to 75 per cent.) of the requisite coal, and adds the remainder afterwards. A portion of the limestone may be kept back likewise. The temperature should be kept up as high as possible. This is evidently the same thing as the Pechiney process, since in the absence of coal an excess of sulphate must be present and only so much cyanide can be formed as corresponds to the nitrogen of the coal added at the end.

Allhusen (No. 3022, July 30, 1878) keeps back 10 per cent. of the total mixture of sulphate, limestone, and coals, which is added shortly before discharging the furnace. This is practically the same as the Pechiney-Weldon process.

Glover (No. 3973, Oct. 9, 1879) adds a manganese salt or oxide in the black-salt pan; this in the calcining-pan forms blue sodium manganate, whose colour blends with the yellow shade of iron-containing ash to give white.

Pauli (Dingl. Journ. ccxxxii. p. 537) adds, before discharging, a mixture of dried fished salts from caustic-soda-making (which always contain much sulphate), or caustic bottoms with slaked lime. This does not seem essentially different from the P.-W. process.

According to a communication which the author has received from Mr. Benker, of Rouen, the final addition of acid sulphate ef soda (nitrecake) ensures a far more complete destruction of the cyanides than that of ordinary sulphate.

CHAPTER VI.

THEORY OF THE SODA PROCESS ACCORDING TO LEBLANC.

When we consider that even the composition of black ash is not quite certain, both on account of the wide differences between the various analyses and of the unavoidable decompositions and re-arrangements of elements in contact with water, we need not be surprised at the discordances between the views held on the nature of the process that goes on in the furnace. The most difficult question was, how is an insoluble compound of sulphur and calcium formed from which the soluble constituents can afterwards be separated by lixiviation? To answer this and other questions is difficult even from the fact that the processes going on in the white-hot furnace admit of observation only by means of some secondary signs, such as the colour of the flame, the appearance of the melting mass, latterly also the analyses of the fire-gas, and because our analyses are necessarily limited to the cooled-down product, in which already on cooling, and still more during the subsequent treatment with water, changes can and must take place.

Besides analyzing the product, we must not neglect the proportions of the mixture which have proved most favourable for the work (see p. 376 *et seqq.*). These ought to permit valid conclusions to be drawn; for on examining the various statements, so far as they are trustworthy, and calculating them upon pure substances, we find very good agreement so far as the process universally used up to the last few years is concerned. We may assume that up to the most recent time, with 100 parts pure sodium sulphate, never very much more nor very much less than 100 parts of pure calcium carbonate and 45 parts of pure carbon were employed. Calculated into equivalents, this means 1 equivalent of Na_2SO_4 to 1·42 of

$CaCO_3$ and 5·32 of C; and it would thus seem as if, for the reaction going on in the furnace, to 2 equivalents of Na_2SO_4 3 of $CaCO_3$ and at least 10 of carbon were necessary. Indeed these proportions are assumed in most of the older theories of the process; but although this may have been justified by the facts then known, it is impossible to make that assumption now, since the experiments made by Gossage, Kolb, and others with only *one* equivalent of $CaCO_3$ to one of Na_2SO_4 have been borne out by the result of Mactear's plan of working in the revolving black-ash furnaces.

The first explanation of the process of soda-making according to Leblanc was given in 1830 by Dumas ('Traité de Chimie,' ii. p. 474), and was accepted in its main features for a long time almost without question. Dumas started from the assumption that CaS is soluble in water, because neither H_2S nor $(NH_4)_2S$ causes a precipitate in a solution of $CaCl_2$, and that consequently any CaS present in black ash on contact with water must decompose with the sodium carbonate into sodium sulphide and calcium carbonate. He therefore rejects the equations*:—

$$1.\ Na_2SO_4 + CaCO_3 = Na_2CO_3 + CaSO_4,$$

$$2.\ CaSO_4 + C_4 = CaS + 4CO;$$

for then on lixiviation the following would happen, viz.:—

$$3.\ Na_2CO_3 + CaS = Na_2S + CaCO_3.$$

For this reason Dumas thinks that but $1\frac{1}{2}$ (instead of 1) equivalent of $CaCO_3$ must be employed in Leblanc's process, so that not CaS, but calcium oxysulphide (2CaS, CaO), as already assumed by Thénard, is formed, which by its insolubility in water retains the sulphur and prevents the appearance of large quantities of Na_2S in the tank-liquor under normal circumstances. He represents the process by the following equation:—

$$4.\ 2Na_2SO_4 + 3CaCO_3 + 9C = 2Na_2CO_3 + CaO, 2CaS + 10CO.$$

This is represented by the following proportions:—

Sodium sulphate	100
Calcium carbonate	105·6
Carbon	38

* Of course all his formulæ have been translated into modern notation.

which, indeed, very closely correspond with the proportions practically used at that time and much later, if the impurities and the unavoidable loss by burning of coal are taken into account.

The same subject in 1847 (and afterwards) was treated by Unger (Ann. Chem. Pharm. lxi. p. 129, lxiii. p. 240, lxvii. p. 78, lxxxi. p. 289). In his earlier publications he takes just the same ground as Dumas; he also assigns, as the reason why on treating the black ash with water the sodium sulphide is not reformed, the formation of an oxysulphide of calcium. To this he gave a formula deviating from that of Dumas, viz. $CaO, 3CaS$, especially because H. Rose had prepared an analogous barium compound. He was not, however, satisfied with a simple equation, such as that proposed by Dumas, but believed that during the furnace process a whole series of reactions take place. First the coal transforms sodium sulphate into sulphide, calcium carbonate into quicklime. On reducing the sulphate, the gas given off consists almost entirely of CO_2, not CO (this has subsequently been confirmed). The sodium sulphide with quicklime yields calcium oxysulphide and sodium oxide; and the latter is alternately transformed by the coal still present and the atmospheric oxygen into sodium carbonate. In his later publication he essentially modified this theory, by ascribing an important part to the steam, formed by the hygroscopic water and the hydrogen of the coal, and contained in the atmospheric air. The steam in contact with the live coals yields hydrogen; this reduces $CaSO_4$ to CaS, which, on igniting with steam, yields H_2S and is partly changed into oxysulphide. The $CaSO_4$ is formed by a partial decomposition of Na_2SO_4 with $CaCO_3$ at a red heat; the remainder of the sodium sulphate is reduced to sulphide, which with Ca_2CO_3 yields CaS, and this again, in a damp flame, oxysulphide. The escaping H_2S is at once taken up by sodium oxide or carbonate; the newly formed Na_2S is decomposed by the $CaCO_3$ in excess, with formation of calcium oxysulphide; and by this play of reactions all the Na_2S is gradually transformed. This very complicated theory is at once refuted by the fact that it is possible to make black ash from perfectly dry materials in a closed crucible, with total exclusion of steam (Scheurer-Kestner, Wagn. Jahresb. 1863, p. 238).

Brown (Philos. Mag. xxxiv. p. 15) does not go so far in theoretical speculations. According to him, there is simply reduction of sodium sulphate, by coal, to sulphide; and this with calcium carbonate yields sodium carbonate and calcium sulphide; the latter

at once takes up lime and forms calcium oxysulphide. He also gives to the latter the formula $CaO, 3CaS$; and his equations thus become:—

$$1.\ Na_2SO_4 + 4C = Na_2S + 4CO;$$

$$2.\ 3Na_2S + 4CaCO_3 = 3Na_2CO_3 + CaO, 3CaS + CO_2.$$

All these theories are founded upon the assumption of the existence of calcium oxysulphide, which Dumas himself never prepared, and the existence of which he only inferred from a reaction indicated by himself, viz. that from a mixture of CaS and Na_2CO_3 in *equivalent* proportions water dissolves Na_2S, whilst, if to this mixture an excess of lime is added, a solution of Na_2CO_3 is obtained.

Now the existence of this reaction has been disputed, and the principal foundation for the calcium oxysulphide theory removed, apparently first of all by Kynaston, on the strength of experiments made in E. S. Muspratt's laboratory in 1858, and described in the latter's 'Chemistry,' ii. p. 924, and by Kynaston himself in the Chem. Soc. Quart. Journ. xi. p. 155. He found that if black ash was left in contact with water for some time, its CaO, inclusive of that contained in the presumed $CaO, 2CaS$ or $CaO, 3CaS$, was completely transformed into $CaCO_3$, whilst $NaOH$ was formed at the same time. Although this did not absolutely disprove the existence of an oxysulphide, it yet showed that such a body could not possess that stability in the presence of water which is the foundation of Dumas's theory. Kynaston inclined towards ascribing the non-decomposition of the sodinm carbonate in black ash to a compound of CaS with $CaCO_3$, the existence of which, however, he has not proved, and it is hardly probable.

Very weighty reasons against the oxysulphide theory were marshalled by Gossage. In his essay, called 'A History of the Soda-manufacture' (read in September 1861, published in 1863), p. 15, he states that already in a patent-specification of the year 1838 he had proved the residue from lixiviating black ash, especially if much water was employed, to consist of a mixture of calcium monosulphide and carbonate, without any sodium sulphide having got into the liquor; in fact, CaS is quite insoluble in water, as is proved by preparing it from gypsum ignited with coal; nor is it much attacked by sodium carbonate; and so far as calcium poly-

sulphurets are formed, these only are dissolved and subsequently form sodium sulphide. The advantage of adding chalk in excess is merely that a larger surface is offered for the reactions, and the operation in the furnace is facilitated, which also prevents the formation of calcium oxysulphides. It must be granted that these theoretical speculations of that experienced practical man have since been entirely confirmed.

Both Kynaston and Gossage proved that in black ash no caustic soda can be present; for on melting caustic soda with calcium carbonate decomposition into caustic lime and sodium carbonate takes place, and, moreover, black ash yields no caustic soda to alcohol. The same black ash, however, on lixiviation with water, yields large quantities of caustic soda, which consequently can only have been formed by the action of quicklime on sodium carbonate; and this could not have happened without a splitting-up of the supposed oxysulphide. Gossage expresses the soda-process as follows:—

$$2Na_2SO_4 + 3CaCO_3 + 9C = 2Na_2CO_3 + 2CaS + CaO + 10CO;$$

but he does not himself believe that all the C goes away as CO, which he assumes only for the sake of simplicity. This formula entirely answers to the proportions indicated by Dumas; but the presence of the third equivalent of $CaCO_3$ is not necessary for the equation, and is only claimed for the practical requirements of black-ash making. According to Hofmann's 'Report by the Juries,' p. 26, Gossage asserts that by the employment of *exactly equivalent quantities* of sulphate and limestone, both on the small and the large scale, he obtained black ash yielding sodium carbonate on lixiviation, and that two other manufacturers, on repeating this experiment on the large scale, had been equally successful. We shall see that Kolb also obtained the same result; and, at all events, Mactear's revolving-furnace process has strikingly demonstrated the correctness of Gossage's assertion.

Scheurer-Kestner (Rép. Chim. appl. 1862, p. 231) also pronounced against the oxysulphide theory. He adopted Kynaston's reasons against the presence of caustic soda in black ash, and added another reason, viz. that otherwise the unlikely assumption that black ash contains anhydrous Na_2O would become necessary. He also argued that the non-existence of caustic soda in black ash, along with the constant presence of this compound in black-

ash *liquor*, proves with certainty the presence of quicklime and the absence of calcium oxysulphide. But he also disproved in a more exact way the existence of the latter by mixing solutions of pure sodium carbonate, of various degrees of concentration, with fresh tank-waste, and daily estimating the caustic soda and sodium sulphide formed. If the lime had been chemically combined with CaS to form an oxysulphide, and the latter had been slowly decomposing, the sodium sulphide must have increased proportionally with sodium hydrate. The experiment most distinctly proved the contrary: the liquor at once became caustic; but its degree of causticity increased very little and rather decreased again (because NaOH itself acts upon CaS), ultimately arriving at zero; the Na_2S, on the other hand, increased steadily day after day, and ultimately remained alone.

In a further publication (Compt. Rend. lvii. p. 1013, lviii. p. 501) Scheurer-Kestner showed (like Gossage) that CaS itself is almost insoluble in water (at 12°·6 C. 1 part is soluble in 12,500 parts of water); on treating pure CaS with a solution of Na_2CO_3, gradually Na_2S and $CaCO_3$ are formed, but not more quickly than on treating black-ash with water. His own idea of the soda-process is this:—First the sulphate is by the coal reduced to Na_2S; and this with the $CaCO_3$ decomposes to Na_2CO_3 and CaS. The latter reaction can be proved independently on a small scale. In practice more than an equivalent of $CaCO_3$ is employed, because a portion of this becomes caustic before the reduction of sodium sulphate to sulphide is complete, and the subsequently formed Na_2S would enter into the liquors as such, if it did not find any $CaCO_3$ for converting it into Na_2CO_3. This point was withdrawn by Scheurer-Kestner in 1867, and Gossage's explanation adopted. During these processes not carbon monoxide, as the previous theorists had stated, but exclusively carbon dioxide is formed; so that the equations run:—

1. $5Na_2SO_4 + 10C = 5Na_2S + 10CO_2$;
2. $5Na_2S + 7CaCO_3 = 5Na_2CO_3 + 5CaS + 2CaO + 2CO_2$ *.

It is true that towards the end of the operation carbon monoxide

* Ferd. Fischer (Deutsch. chem. Ges. Ber. ix. p. 1559) indeed found no CO in the gases of a black-ash furnace, but merely CO_2, along with 3·3 to 2·6 per cent. oxygen.

is given off, as proved by the flames issuing from the mass, which afford such a valuable sign of the finish; but as in the reduction of sulphate, according to his own and Unger's experiments, next to no CO is formed, but almost exclusively CO_2, the CO-flames at the end of the operation, when the temperature is much higher, must arise from the action of coal on the limestone in excess:—

$$3.\ CaCO_3 + C = CaO + 2CO.$$

It is well known that the ball must be drawn after the evolution of CO has begun and before it is finished; and the excess of limestone permits the employment of this practical sign. Dubrunfaut assented to these views, and asserted that he had come to the same conclusion thirteen or fourteen years previously (Bull. Soc. Chim. 1864, i. p. 346). His formula is

$$Na_2SO_4 + CaCO_3 + 4C = Na_2CO_3 + CaS + 4CO;$$

but this again adopts the erroneous assumption that CO, not CO_2, is the gaseous product of the reaction.

The calcium oxysulphide still had its advocates. On the strength of many analyses of tank-waste from one and the same factory, at Dieuze, E. Kopp (Compt. Rend. lxi. p. 560) concluded that in it lime and sulphur existed in the proportion indicated by Dumas, viz. CaO, 2CaS. Scheurer-Kestner (ib. p. 640) replied that this proportion varies in the tank-waste of different works and depends upon the original mixture. Kopp then (ib. p. 796) adduced somewhat more weighty reasons in favour of Dumas's theory. On trying the reaction upon solutions of sodium carbonate (1st) of pure lime, (2nd) of a quantity of soda-waste which, according to analyses, contained exactly the same quantity of calcium hydrate (viz. 12 per cent.), much more caustic soda was obtained in the first than in the second case. [This experiment, apparently performed only once, is not very conclusive when the difficulty of stating the precise quantity of $Ca(OH)_2$ to be assumed in such a complicated mixture as tank-waste is taken into account; moreover Pelouze (Compt. Rend. lxxii. p. 315) points out that Kopp's analysis of tank-waste is altogether abnormal, and that probably some error had occurred.]

Kopp further found that, on treating equal volumes of solution of sodium carbonate, first with pure CaS, secondly with the corresponding quantity of soda-waste, more sodium sulphide was formed

in the first than in the second case. [The above criticism is applicable to this point also.] Lastly, Kopp also found [it appears, in a single experiment] that from a nearly neutral solution of manganous chloride manganese protoxide (which is precipitated by free lime) could not be precipitated by his [abnormal] soda waste, nor yet by an artificial mixture of 2CaS and 1CaO. From this it would appear as if the oxychloride could be simply compounded from its constituents with the assistance of water.

Since Kopp, only P. W. Hofmann has tried to uphold the existence of calcium oxysulphide (Compt. Rend. lxii. p. 291). He calcined 2 equivalents of gypsum with 1 equivalent of free lime and coal; the product could not causticize sodium carbonate; and he therefore adopted Kopp's conclusion as to the existence of such a compound in soda-waste. Both his experiment and conclusion were completely refuted by Pelouze (Compt. Rend. lxii. p. 315). Apart from pointing out that even the existence of an artificially prepared calcium oxysulphide would not prove its presence in soda waste, Pelouze showed that, in the experiment of P. W. Hofmann, at a moderate temperature the CO_2 formed by the reduction of gypsum combines with the lime, and a mixture of calcium sulphide and carbonate remains, which, of course, cannot causticize sodium carbonate. If, however, the experiment be performed at such a high temperature that the $CaCO_3$ is decomposed into CaO and CO_2, the resulting mixture of CaS and CaO readily causticizes soda. [This experiment at the same time refutes Kopp's above-quoted experiment with a mixture of 2CaS and CaO, and, as Kopp made no reply, must be considered decisive.] Otherwise Pelouze substantially confirmed Scheurer-Kestner's results concerning the absence of NaOH or Na_2O from black ash, and the unequal progress of the formation of Na_2S and NaOH on lixiviation, and concludes decidedly that the assumption of calcium oxysulphide in black ash is neither necessary nor allowable. For this he adduced the novel fact that on treating equal quantities of black ash, one with tepid, and the other with boiling water, in both cases an equal quantity of caustic soda was formed, but much more Na_2S in the second case, with less Na_2CO_3,—and that the quantities of H_2S and CO_2 expelled from washed tank-waste by an acid suffice for completely saturating all the lime, which could not be the case if a stable calcium oxysulphide were present and the caustic soda of the tank-liquor had been formed only at the expense of some free

lime present in excess, as is necessarily assumed by those who adhere to the oxysulphide theory. Exactly the same result was obtained by Petersen (Wagner's Jahresb. 1866, p. 164), who likewise adopted the views of Scheurer-Kestner.

Much more conclusive than any isolated experiments made with some odd sample of soda-waste are the exhaustive researches made by Kolb (Ann. Chim. Phys. [4] vii. p. 118). He operated on the large scale in a good furnace, in which he fluxed two mixtures of chalk, sulphate, and coal—one (A) corresponding to Dumas's formula, the other (B) to that of Dubrunfaut. If the formation of an oxysulphide is indispensable, the mixture A ought to furnish black ash free from Na_2S and saturated with CO_2, but B nothing but Na_2S *. If, however, no oxysulphide is formed, but calcium sulphide itself is insoluble in the alkaline liquor, the results of the two operations will differ in this respect; the liquor A, owing to the excess of chalk and coal, will be more caustic than B. Now the products, lixiviated precisely in the same manner, yielded (from 100 parts of sulphate):—

Mixture A.

167·5 black ash of 38° Decroiz.
70·7 soda ash of 90° „

$$\text{viz.}\quad \left.\begin{array}{r} 52{\cdot}60\ Na_2CO_3 \\ 8{\cdot}45\ Na_2O \end{array}\right\} = 66{\cdot}9\ Na_2CO_3$$
$$\begin{array}{r} 0{\cdot}15\ Na_2S \\ 0{\cdot}93\ Na_2S \end{array}$$

Mixture B.

134·0 black ash of 47° Decroiz.
77·5 soda ash of 81° „

$$\text{viz.}\quad \left.\begin{array}{r} 59{\cdot}51\ Na_2CO_3 \\ 3{\cdot}39\ Na_2O \end{array}\right\} = 65{\cdot}3\ Na_2CO_3$$
$$\begin{array}{r} 2{\cdot}16\ Na_2S \\ 6{\cdot}71\ Na_2SO_4 \end{array}$$

* Landolt, in his extremely lucid report in Hofmann's Bericht, 1875, i. pp. 421, 468, points out that Kolb in this case has misinterpreted his own experiments. There is no reason why, if a calcium oxysulphide exists, it should not be formed in the mixture B. Only in this no more than two thirds of the sodium sulphate would be converted into carbonate, one third remaining as sulphide, thus:—

$$3Na_2SO_4 + 3CaCO_3 + 12C = 2Na_2CO_3 + Na_2S + CaO, 2CaS + 12CO + CO_2.$$

Thus Dubrunfaut's formula [apart from the formation of CO] had been completely confirmed; B could only contain sodium carbonate and calcium sulphide, which on lixiviation are not mutually decomposed. That this is not the case, Kolb proved by special experiments. Strong solutions of soda ash after forty-eight hours' contact with calcium sulphide in large excess in the cold only showed a formation of sodium sulphide to the extent of 1·8 to 2·4 per cent., and after four hours' boiling 3·2 to 4·2 per cent. Solutions of caustic soda only showed traces of a reaction on calcium sulphide. Pure water in forty-eight hours dissolved in the cold 0·23 per cent., in four hours' boiling 0·27 per cent. CaS. This proves that for making black ash only exactly equivalent quantities of Na_2SO_4 and $CaCO_3$ are required. As far as the coal is concerned Kolb adopts Ungerer's view, that CO_2 alone is formed—and no CO, as Dubrunfaut supposes. He consequently changes the latter's formula to

$$Na_2SO_4 + CaCO_3 + 2C = Na_2CO_3 + CaS + 2CO_2,$$

corresponding to 100 Na_2SO_4, 70·4 $CaCO_3$, and 17 C, yielding (theoretically) 74·6 Na_2CO_3. On carrying out an operation according to this mixture in the furnace Kolb only obtained 43·8 Na_2CO_3; half of the sulphate had remained undecomposed. When the quantity of the coal was doubled, he obtained a practically sufficient decomposition, viz. 65·3 Na_2CO_3, along with 2·16 Na_2S. When, moreover, the quantity of chalk was increased to 101 $CaCO_3$, he obtained 70·1 Na_2CO_3 and only 1·2 Na_2S. He explains the favourable action of an excess of chalk in just the same way as Gossage and Scheurer-Kestner had done; that of the excess of coal, not from a formation of CO on the reduction of sodium sulphate (for the experiment shows that 100 parts of sulphate are actually completely converted into sodium sulphide with evolution of CO_2), but from the fact that coal is spent in another way, viz. in forming CO with $CaCO_3$ [as Scheurer-Kestner had already stated; moreover, recently less than 30 per cent. of coal has in practice been found sufficient]. According to special experiments by Kolb, chalk is decomposed by coal at a moderate red heat with evolution of CO, at the same temperature at which sulphate yields CO_2 with coal, whilst chalk heated by itself splits up only at a much higher temperature into CaO and CO_2. The coal consequently acts in the furnace at the same time on the sulphate and

the chalk, giving off a mixture of CO and CO_2; since during the reduction of sodium sulphate to sulphide the chalk is converted into quicklime, and the former no longer meets with calcium carbonate, the reaction cannot be (as usually represented) thus—

$$Na_2S + CaCO_3 = Na_2CO_3 + CaS.$$

If this were correct, a black ash not fluxed sufficiently long would contain much unchanged Na_2S, which is not the case. In two experiments,

1st. A *finished operation* yielded :—

162 black ash with 42° Decroiz.

73·8 soda ash with 88° Decroiz,

$$\text{viz.}\quad \left.\begin{array}{r} 64{\cdot}20\ Na_2CO_3 \\ 4{\cdot}72\ Na_2O \end{array}\right\} = 72{\cdot}2\ Na_2CO_2$$

$$\begin{array}{r} 1{\cdot}12\ Na_2S \\ 2{\cdot}06\ Na_2SO_4 \end{array}$$

2nd. A *prematurely interrupted operation* yielded :—

170 black ash of 32° Decr.

82 soda ash of 70° Decr.,

$$\text{viz.}\quad \left.\begin{array}{r} 48{\cdot}60\ Na_2CO_3 \\ 3{\cdot}26\ Na_2O \end{array}\right\} = 54{\cdot}2\ Na_2CO_3$$

$$\begin{array}{r} 0{\cdot}85\ Na_2S \\ 25{\cdot}41\ Na_2SO_4 \end{array}$$

In order to prove that the CO_2 of the chalk does not take any part in the formation of black ash, because it is driven off at the same time as the sulphate is reduced, Kolb tried replacing the chalk by quicklime, and obtained almost exactly the same black ash as with chalk. Nor is the CO_2 given off by the reduction of the sulphate sufficient for supplying that of soda ash; for by experiments with the ordinary black-ash mixture in a closed crucible he only obtained 12·45 Na_2CO_3 (inclusive of NaOH) along with 35·30 Na_2S and 18·40 Na_2SO_4. He concludes that the CO_2 of the fire-gases is the principal agent; the same mixture which yielded such bad results in a crucible, gave excellent results when it was ignited in a fireclay pipe and CO_2 conducted through the pipe during the operation.—Kolb's experiments (described in the same place) on the stirring of the mass, the temperature, the kind and the excess of carbon are of less importance for the theory of the soda-process, and are therefore cited each in its proper place. As the

final result of his work, Kolb states the following three equations, representing as many reactions simultaneously taking place in the black-ash furnace:—

1. $Na_2SO_4 + 2C = 2CO_2 + Na_2S$;
2. $CaCO_3 + C = 2CO + CaO$;
3. $Na_2S + CaO + (CO_2 \text{ in excess}) = Na_2CO_3 + CaS$.

That and why these proportions cannot be exactly observed in practice, but an excess, not too large, of chalk and coal must be employed, has been sufficiently explained in the foregoing. The CO formed according to the second equation is at once burned into CO_2; but Kolb does not ascribe to this the well-known flame reaction at the end, as Scheurer-Kestner had done, but to the action of coal on finished sodium carbonate, sodium oxide being formed ($Na_2CO_3 + C = Na_2O + 2CO$). [This last portion of Kolb's reasoning rests on a very weak foundation; for, 1st, why are the flames only noticed at the end, if there is a formation, and consequently a combustion, of CO from the first? 2nd, the existence of sodium oxide in black ash has never been proved; on the contrary, Pelouze (*l. c.*) found that black ash, moistened with a little water for some time so that any Na_2O must have been converted into NaOH, yielded no NaOH to alcohol.]

Kopp's last observations (p. 433) were also impugned by Scheurer-Kestner (Compt. Rend. lxiv. p. 615). He states, in accordance with Kolb, that the calcium-oxysulphide theory is entirely exploded; but he controverts Kolb's assertion that the calcium carbonate loses its CO_2 by the action of the coal, and the formation of sodium carbonate is only possible by the action of the fire-gases, and that in crucibles no black ash can be made. He on his part obtained very good black ash, both in fireclay and platinum crucibles; his most convincing experiments were made with porcelain crucibles, closed by lids tied down with copper wire and plunged into liquid black ash at the moment when a ball had been drawn. Thus they were heated to the proper temperature and protected from the fire-gases; and after the cooling of the ball they were recovered by breaking it up. In this way he obtained from a mixture of 100 sulphate, 70 calcium carbonate, and 17 charcoal porous lumps having the appearance of ordinary black ash, which on lixiviation yielded soda ash containing sometimes 92 per cent. Na_2CO_3. It is consequently established that black ash can be made in crucibles without any assistance from

the fire-gases. The same result was obtained with an excess of calcium carbonate; and the soda ash was free from caustic, which proved that the $CaCO_3$ had not been decomposed. The following experiments directly contradict Kolb's statements:—Three crucibles were dipped into the same liquid black ash, one of them containing the ordinary black-ash mixture, the other pure calcium carbonate, the third a mixture of 50 grams $CaCO_3$ with 6 grams coal. After the operation the first crucible contained black ash; the contents of the two others were unchanged; consequently, contrary to Kolb's assertion, the decomposition of calcium carbonate, even in the presence of coal, must require a higher temperature than the reduction of sodium sulphide. It is quite correct that black ash can be obtained with quicklime as well, not merely in the furnace where the lime meets with sufficient CO_2 to be converted into carbonate, but also in crucibles, where the reduction of the sulphate by coal furnished the CO_2; but no caustic soda is formed, and there is consequently no reason whatever for attributing any part to the CO_2 of the fire-gases in the ordinary black-ash operation. The question is completely decided by the fact that on directly heating sodium sulphide with calcium carbonate black ash is obtained.

According to Scheurer-Kestner the following processes go on in the black-ash furnace. The mixture occupies a depth of several inches on the furnace-bed. Its upper portions are first reduced, and that to a considerable extent before the surface is renewed by working with the tools. The quicklime which had formed in the pasty layer at the surface is again converted into carbonate by the CO_2 arising from the reduction of sulphate in the lower layers. At the moment when the sodium sulphide fuses, it penetrates the chalk, and they are mutually decomposed. When all the sulphate has been reduced and the evolution of CO_2 becomes less, the temperature of the mass rises and the calcium carbonate in excess begins to decompose with evolution of CO. The evolution of this gas is a valuable sign for marking the completion of the operation. Since it only occurs when the mass begins to stiffen, it imparts to it that porosity so valuable for lixiviation. If the carbon required for the reduction of the sodium sulphate and the decomposition of the chalk be taken into account, the reaction may be expressed by the following three equations:—

Phase 1. $5\,Na_2SO_4 + 10\,C = 5\,Na_2S + 10\,CO_2$;

„ 2. $5\,Na_2S + 5\,CaCO_3 = 5\,Na_2CO_3 + 5\,CaS$;

„ 3. $2\,CaCO_3 + 2\,C = 2\,CaO + 4\,CO$.

[Of course in the third phase it cannot be of importance that just two equivalents of calcium carbonate be decomposed; less than that will be quite sufficient.]

The author confesses that he considers the theory of the black-ash process established by the researches of Scheurer-Kestner, which have never been refuted during the last ten years, and that he agrees with him in every particular. In Mactear's revolving-furnace process the third of the above-mentioned phases is not carried out, but replaced by the direct addition of quicklime.

Mactear has latterly (Chem. Soc. Journ. 1878, xxxiii. p. 475) tried to prove that in the reduction of the alkaline sulphates by carbon at "more than red heat" CO_2 is not formed, but merely CO, and that even at a dull red heat about 1 mol. of CO to 4 mols. of CO_2 is given off. His conclusion, which is in opposition to the above-stated direct experiments of Unger, Gossage, Scheurer-Kestner, and Kolb, is based only on indirect assumptions from the analysis of the residue, and not supported by any analysis of the gases evolved in the process. This matter has been thoroughly investigated in the author's laboratory by Mr. J. Arnold Fischer (whose research will be published *in extenso* hereafter), with the result of refuting Mactear's assertions, if these are intended to refer to temperatures similar to those of a black-ash furnace, and in most parts confirming the statements of the previous investigators. His experiments were made by heating a mixture of pure sodium sulphate and the purest carbon obtainable in a current of dry nitrogen gas, entirely free from oxygen, in porcelain tubes. The escaping gases were passed through absorbents for CO_2 and CO; and the residue was carefully analyzed. Fifteen experiments were made, at different temperatures, viz.:—1st, between the melting-points of antimony and aluminium; 2nd, between the latter and the melting-point of silver; 3rd, between the latter and that of copper; 4th, above the melting-point of copper, at the highest temperature obtainable in the porcelain tube by a coke fire, when at last even the enamel softened and the temperature was at least far above that of a black-ash furnace. At a good red heat, but below the melting-point of silver, the formation of CO was extremely slight, as shown in this table:—

(1) Antimony melted, aluminium not melted.

	I.	II.	III.	IV.
C as CO gas	trace	0	1·62	2·05
C „ CO_2 gas	4·35	18·16	52·67	74·66
C „ Na_2CO_3 (residue)	not estimated	4·08	9·25	2·47
C unchanged („)	„	79·31	34·03	17·83

(2) Aluminium melted, silver not melted.

	V.	VI.	VII.
C as CO	0·79	0·14	1·29
C „ CO_2.........................	85·70	82·98	86·52
C „ Na_2CO_3	2·91	1·96	not estimated
C unchanged	10·67	13·56	„

Between the melting-points of silver and copper, *i. e.* at a temperature very similar to the ordinary heat of a black-ash furnace, sometimes very little, sometimes rather more CO was formed, but never beyond one seventh of the CO_2, as shown by the following table:—

	VIII.	IX.	X.	XI.	XII.
C as CO	2·01	1·47	10·75	11·71	8·98
C „ CO_2	82·25	88·09	79·21	75·89	74·90
C „ Na_2CO_3	7·54	2·03	not est.	8·28	6·41
C unchanged	7·70	7·80	„	4·01	6·14

Nor was Mactear's statement confirmed even at an intense white heat, when copper was readily melted, as shown by this table:—

	XIII.	XIV.	XV.
C as CO	9·59	0·60	0·40
C „ CO_2	85·06	79·23	86·34

These experiments, where the carbon dioxide was collected as such, are all the more conclusive as other experiments proved that pure sodium sulphate was *completely* reduced by heating it to the melting-point of silver in a current of pure carbon monoxide, whereby of course CO_2 was formed. Along with the principal product, Na_2S, sodium polysulphide and carbonate were always formed, both in much larger quantities at lower temperatures than at higher ones. Also sodium sulphite was always found, but not in large quantities, and independent of the degree of heat employed. We may therefore take it as established that the principal products of the decomposition of sodium sulphate by carbon are (as they have hitherto been assumed to be) sodium sulphide and carbon dioxide.

CHAPTER VII.

BLACK ASH AND TANK-LIQUOR.

Black Ash.

The work in the ball-furnace is tested in the first place by carefully examining each ball, at first outside, then after breaking it up. In many works every ball, before being tilted out, is weighed in its bogie in order to see whether any large portion of it has been left behind in the furnace. In all cases a laboratory testing follows, but to very different extents in different works.

The balls ought to weigh about $1\frac{3}{5}$ times as much as the sulphate employed. A ball made from 3 cwt. of sulphate ought to weigh from 4 cwt. 2 qrs. 21 lb. to 4 cwt. 3 qrs. 14 lb. Stohmann (Kerl-Stohmann's Techn. Chemie, 3rd ed. v. p. 350), experimenting with 16 hand furnaces and one revolver, obtained from the former, with a charge of 100 sulphate, 97·5 dry chalk, and 59·1 coal:—

Per cent. by weight (on the sulphate)...	154·8	156·1	156·4
Soluble per mille	467·7	457·3	467
Insoluble per mille	581·0	582·0	587
Total	1048·7	1039·3	1054

From the revolving furnace:—

(Charge 100 sulphate, 97·5 chalk, 55 coals)

Per cent. by weight (on the sulphate)...	157·6	163·6	164·3
Soluble per mille	452	451	447·7
Insoluble per mille	571	573	576·8
Total	1023	1024	1024·5

A *properly made ball* is easily detached from the bogie. In the places exposed to the air at a red heat, especially at the surface projecting from the bogie, it has a liver-brown colour, at the other surface a blackish-brown one. On breaking, a good ball presents

a slate-grey colour and a honeycombed, almost pumice-like structure; it ought to be as homogeneous as possible, with only a few particles of coal here and there, but no black streaks (from coal) or white ones (from chalk); these testify of bad working. Many dispersed particles of coal, or of chalk, prove that there was an excess. The colour is not quite so satisfactory if it has any pink or purple shade. The inside of a ball ought to be all of one shade, except close to the edge, where it is always a little darker.

Balls which on the outside, before breaking up, are quite *black* instead of slate-grey, blackish brown, or blackish grey, are nearly always very bad. Either they have not been long enough in the fire, or they have not been sufficiently wrought. In this case on breaking them a large number of pieces of coal are noticed all over. Of course this appearance might also be caused by too much coal in the mixture; but then all the balls, and not a few only, would show it, and it would also distinctly come out in the furnace, where the coals would not all be burnt and the ball would not become "clear." As the more coal the more trouble the men have in clearing the ball, there is little fear that they will surreptitiously put too much coal in the mixture, and black balls can only be ascribed to bad work on their part,—provided the furnace was hot enough; for otherwise the black ash never becomes "clear."

Balls which on the outside have a *very dense appearance and pale pink spots* are very suspicious; certainty is only gained by breaking them up. In the worst cases they are brick-red, in milder cases pink or purple all over or in streaks. This always comes from overheating the ball and leaving it too long in the furnace, and is the men's fault. Such *red* or *burnt* balls occur much more readily if the mixture contains only a bare sufficiency of chalk than if the latter is in excess. Consequently it is the man's interest to use as much chalk as possible in the mixture, because his balls will not be so easily burnt; but it is the manufacturer's interest to limit the chalk to the smallest possible quantity, much less on account of its price than because all the more soda is lost in an insoluble form the more chalk has been used for the mixture. The manufacturer will therefore have to make out by careful experiments with what minimum of his chalk or limestone good balls can be turned out, and will fix this as the proportion for mixing; the furnaceman certainly will then have to be much more careful in his work and turn over the mass much better in order not to leave any sodium sulphide

(which gives the red colour); especially he will have to bestow the greatest care upon observing the proper moment for drawing his ball—not a minute too soon, lest it be black, nor a minute too late, lest it be red. With more chalk the transition is not so sudden, and the work is consequently easier, at the expense of the yield of soda ash.

Since a limestone mixture is finished more easily and at a lower heat than a chalk mixture, the furnacemen on changing from one material to the other must first have a little practice before they can turn out good balls. That burnt balls occur much less frequently when the mixing-coal is cut down to a minimum, has been mentioned before.

A burnt (red) ball on testing always shows much sodium sulphide, along with sulphate. The latter may arise partly from the burning of sodium sulphide, partly from that of calcium sulphide into sulphate, which on dissolving decomposes sodium carbonate. Burnt balls are also too dense, and cannot be completely exhausted on lixiviation. Hargreaves (Chem. News, xv. p. 232) ascribes the red colour to an allotropic modification of sodium sulphide which does not act on limestone; this modification is not converted into sulphate by passing chlorine gas through a solution of a red ball, but decomposed with precipitation of sulphur.

Scheurer-Kestner (Bull. Soc. Chim. 1862, i. p. 172) asserts that the red spots consist principally of Na_2S_2, and that they are formed by the action of calcium sulphide upon sodium carbonate at a high temperature:

$$2\,CaS + Na_2CO_3 = Na_2S_2 + 2\,CaO + CO.$$

According to experiments made by Kolb (see last Chapter) "burnt" black ash of a brick-red colour contained an abnormal quantity of sodium sulphide and caustic, viz.

$$\left.\begin{array}{l} 50{\cdot}1\ Na_2CO_3 \\ 10{\cdot}6\ Na_2O \end{array}\right\} = 68{\cdot}3\ Na_2CO_3$$
$$7{\cdot}5\ Na_2S$$
$$0{\cdot}2\ Na_2SO_4.$$

According to him, on heating the ball too much the following happens: if, after once the sodium carbonate has been formed, the mass is heated further with the excess of coal still present, anhydrous sodium oxide is formed and CO escapes, giving rise to the well-known flames ($Na_2CO_3 + C = Na_2O + 2\,CO$); nay, even metallic sodium may be formed and evaporated. Unless the mass is at once

withdrawn from this new reaction, the sodium oxide decomposes calcium sulphide, so that CaO, Na_2S, and even Na_2S_2 are formed ($Na_2O + CaS = Na_2S + CaO$). The Na_2S is afterwards found in the liquor; the lime on lixiviation transforms a corresponding quantity of soda into caustic. Kolb's theory would explain why in the Pechiney-Weldon process, where there is no excess of coal at the end, the burning of balls does not occur in spite of greater heat and longer exposure.

The following table (by Kolb) shows clearly the progress of this reaction as the temperature rises. A mixture of 100 Na_2SO_4, 100 $CaCO_3$, 55 C, gradually heated during an hour from 900° to about 1170°, gave the following results :—

	1.	2.	3. (Silver melted.)	4.	5.	6. (Copper melted.)
Na_2CO_3	10·0	14·2	25·8	14·0	7·0	0·2
Na_2O	0·5	0·7	1·9	7·0	7·0	8·3
Na_2S	0·3	0·6	0·9	6·9	11·8	15·8
NaS_2	0·0	0·0	0·1	0·0	0·0	0·0
$Na_2S_2O_3$	0·0	0·0	0·4	0·6	0·9	1·6
Na_2SO_4	26·6	23·2	10·3	3·5	3·2	1·6

The temperature close to the melting-point of silver consequently seems the most favourable for the success of the operation; generally, the mass ought to be kept between the fusing-point of bronze and that of silver (comp. Fischer's direct pyrometrical estimations, p. 394).

According to Hill (Chem. News, xxx. p. 35) the temperature in the cylinder furnace is much lower than in a hand-furnace; and just for this reason the black ash made in it is so hard and dense that it cannot be lixiviated without the presence of quicklime, which on meeting with water is slaked with an increase of volume, and thus causes the balls to burst. Probably in the cylinder furnace the temperature of forming quicklime from calcium carbonate by the assistance of coal is barely reached, whilst in the hand-furnace it is exceeded. In no case will the temperature, under normal conditions, be so high as to fuse the sodium sulphate itself; and just for this reason the hard fluxings from decomposing-furnaces are so difficult to treat in the black-ash furnace. This also explains why in the still lower temperature of the revolver the sulphate must be employed in a state of fine division.

We have seen before (p. 372) that a higher temperature is advantageous for the destruction of cyanogen compounds.

A kind of balls rarely seen in England, but more frequently on the Continent, are *white* ones. These are caused by an excess of chalk, sometimes by insufficient heat in the furnace inducing the men to employ more chalk in order to prevent the balls from becoming red.

Altogether bad are those balls which, because they have not been sufficiently heated, have never got beyond the state of a comparatively thin liquid, have become stiff, and in consequence of this, instead of exhibiting a uniformly porous, pumice-like mass, appear densely fluxed, mostly much too dark, or purple, in the fracture. Such balls, in England called *soft* balls (although after cooling they are much harder than the good ones), exhibit in the laboratory a bad quality, much sulphate and sulphide especially; and, above all, they are very difficult to dissolve, owing to their dense structure: either a considerable portion of the soda is lost in the residues, or, if this loss is sought to be lessened by employing hot water, a large quantity of sodium sulphide gets into the liquor.

Soft balls are sometimes not owing to any fault of the furnaceman, viz. when a furnace has not sufficient draught and consequently cannot be made hot enough.

The black ash from cylinder furnaces (*revolvers*) has a very different appearance from that made in hand-furnaces. It is very dense on breaking-up, not porous, and externally much lighter. In lixiviation it must be treated in quite a different way.

It is usual for the foreman to take a piece from every ball of each man, fairly representing its average quality; and this is taken to the laboratory for a *chemical examination*. At large works it is, of course, impossible to test every single ball; but at least each man's work is daily tested. At many works each sample is tested alkalimetrically; by itself this is of little value, since the worst contamination, the sulphide, is found as "available alkali." In any case, therefore, the sulphide and the sulphate have each to be estimated separately. Very accurate analyses are out of place here, since the information gained thereby bears no proportion to the time employed. In daily practice it is simply impossible to draw really *exact average* samples of each ball; and since in this respect a very rough approximation has to suffice, the exact analysis of the samples obtained has no meaning. Altogether, the analysis of black ash, which is not an article of trade, in daily practice can only be useful as a means for checking the men. A practised eye, even by

superficially examining the balls before and after breaking, judges of their quality with a considerable amount of certainty; and, indeed, this examination by inspection, to which all balls must be subjected, is of greater importance than the chemical testing, inasmuch as the ball is looked at all over, and the same error cannot happen as that which arises in chemical testing from an accidental divergence of the sample from the average quality. Moreover, in regard to chemical testing, simple and expeditious methods, permitting a large number of tests to be made, are much more useful than more accurate but tedious ones. From this point of view the following prescriptions are framed.

Ten grams of black ash are pulverized and put in a flask containing up to a mark 205 c. c., 5 c. c. of which correspond to the volume of the black ash. It is treated with tepid distilled water, and then shaken for a quarter of an hour, so as to dissolve all the soluble constituents. As many samples have to be treated in one day, a small shaking-machine for a number of bottles at a time is very useful. After sufficient shaking, the flask is filled up to the mark with water, and the liquid is allowed to settle down, which is soon done. Now the clear liquid is poured off; and at least 20 c. c. (=1 gram substance), in case of need more, is employed for the following tests. It is rarely necessary to test for carbonate and caustic, except for special purposes. The general alkalinity is best found by first supersaturating with standard acid, then adding litmus, and titrating for blue with standard alkali; on direct titration the H_2S destroys the colouring-matter of litmus. All this is avoided by employing amidoazobenzene or a similar azo-compound as indicator (Vol. I. p. 48); in this case sodium carbonate may be employed as the standard alkali. Mostly it is sufficient to test for sodium sulphide and sulphate; sulphite or hyposulphite in fresh black ash only occurs in traces, if at all. For sodium sulphide an ammoniacal decinormal solution of zinc nitrate is very convenient; the end of the reaction is found by placing a drop of the liquid on a piece of filtering-paper next to a drop of an alkaline lead solution. Each c. c. of the zinc solution corresponds to 0·1 per cent. (accurately 0·0975) Na_2S, if 20 c. c. of the black-ash solution, containing 1 gram black ash, has been employed. More than ½ per cent. ought never to be present; if that amount be exceeded, the eye will immediately detect a pink colour in the black ash.

Even more accurate than the zinc process is that of Lestelle

(Compt. Rend. lv. p. 739), founded upon the insolubility of silver sulphide and the solubility of all other silver compounds in ammonia. A standard solution of ammoniacal silver nitrate is made by dissolving 27·69 grams of pure silver in pure nitric acid, adding 250 c. c. of ammonia, and diluting the whole to a litre. Each c. c. of the liquid then corresponds to 10 milligrams of Na_2S. The substance to be analyzed is dissolved in water, ammonia added, the liquid heated to the boiling-point, and the ammoniacal silver solution run in, drop by drop, from a burette divided into tenths of a c. c., which causes a black precipitate of Ag_2S. When the reaction is nearly finished, the liquid is filtered, and to the filtrate silver solution again added, till, after repeated filtration, a drop of the clear filtrate is rendered only very slightly turbid by the reagent. If the quantity of sulphide is very small (for instance, in calcined soda ash), the silver solution must be diluted to one half. The process is rapid and exact; and Fresenius has shown, contrary to Kynaston's assertion, that it yields good results even in the presence of sulphites and hyposulphites, as the silver solution is precipitated by Na_2S, before these salts have an opportunity of acting on the silver.

Undoubtedly the most convenient process for estimating the soluble sulphides in black ash is the titration of the solution, diluted and acidulated with sulphuric acid, by *potassium permanganate*, introduced by Scheurer-Kestner (Rép. Chim. Appl. 1863, p. 19). By this, as well as by a *solution of iodine*, the lower oxides of sulphur are oxidized as well; but for the daily practice this is of the less consequence, as in all probability these oxides are formed by the action of atmospheric oxygen on the sulphide. A process proposed by Verstraet (Compt. Rend. lx. p. 348), founded upon the application of cuprammonium nitrate, does not seem to offer any special advantages.

It is even more important to test for *sodium sulphate* than for sulphide in black ash, since it is not betrayed by the colour. This can be done with extreme rapidity in the following manner:—On a test-tube a mark is made for 10 and another for 20 c. c. (or, better, if it is long enough, one for 20 and another for 30 c. c.). The black-ash solution is poured in up to the first mark, supersaturated with pure hydrochloric acid, a little barium chloride added, and the tube filled to the second mark. If the black ash was very well made, no turbidity at all will appear; a slight opalescence does not matter very much;

but if there is any considerable precipitate formed, it is compared with three corked test-tubes, containing 1, 2, and 4 milligrams of Na_2SO_4 with HCl and $BaCl_2$ in 20 or 30 c. c. of liquid. These test-tubes must, of course, be shaken up every time before use. Should the precipitate in the black-ash solution be even more copious than that produced by 4 milligrams of Na_2SO_4, the liquid is diluted till its turbidity corresponds to one of the three standard tubes, the volume now occupied is measured; and thus (roughly it is true, but with practically sufficient accuracy) the percentage of sulphate in the black ash is found. Some works employ Wildenstein's plan—titrating with standard $BaCl_2$ solution till a filtered sample will yield no more precipitate with $BaCl_2$. The result is, of course, more exact; but the time taken by the test is much longer than by the plan above indicated.

The testing for *cyanides* will be described afterwards, in treating of tank-liquor.

The composition of black ash has been very frequently examined; and we give, in the subjoined table (p. 450), a synopsis of a number of analyses. But we must point out that most of the published analyses are not worth much. In the first place, with but few of them is it stated whether the black ash has been examined in a completely fresh state or whether it has been exposed to the air for any length of time previous to analyzing it—which produces rapid changes in it. Then it must also be remembered that on the addition of water considerable action takes place, and the constituents of black ash group themselves very differently, according to the kind of action, the quantity and temperature of the water, and the duration of the treatment. This especially holds good of the proportion of sodium hydrate. Further, most analyses take no notice of the established fact that a very sensible quantity of sodium compounds is always present in insoluble form; and an analysis not showing these cannot be accurate.

In these analyses the hypothetical calcium oxysulphide, quoted by some authors, but now generally assumed to be non-existent, has been accounted for under its constituents CaS and CaO. The silica by some is divided among the bases, by others stated separately, but is of course never to be understood as present in the free state (sand being given separately). Apart from calcium oxysulphide, the compounds have been grouped in the same way as is done by the analysts themselves. Beside the compounds

	1.	2.	3.	4.	5.	6.	7	8.	9.	10.	11.
	Ringkuhl near Cassel. (Unger.)		Liverpool. (Murphy.)	(Muspratt & Danson.)	(Kynaston.)	Newcastle. (Richardson.)	Glasgow. (Brown.)	Jarrow Hand-furnaces. (Stohmann.)		Jarrow Revolvers. (Stohmann.)	Amiens. (Kolb.)
Sodium carbonate	23·57	37·8	41·49	28·89	36·88	9·89	35·64	44·41	38·45	43·27	44·79
„ hydrate	11·12	1·6	......	8·27	......	25·64	0·79	......	3·17	......	......
„ silicate	......	......	1·16	......	1·18	......	......	......	......	......	1·52
„ aluminate	......	......	0·39	......	0·69	......	2·35	......	......	......	1·44
„ sulphate	1·99	......	0·75	0·82	0·39	3·64	1·16	1·54	1·54	1·06	0·92
„ chloride	2·54	0·4	1·31	3·07	2·53	0·60	1·91	1·42	1·75	1·48	1·85
„ sulphide (Na_2S)	......	......	......	0·40	......	......	1·13	......	......	......	......
Calcium oxide	7·16	19·7	9·32	9·24	9·27	7·32	12·30	10·44	10·18	7·13	9·68
„ sulphide (CaS)	27·60	28·8	33·19	25·86	28·68	28·25	23·17	28·87	27·34	27·73	29·96
„ carbonate	12·90	......	0·86	14·22	3·31	15·67	......	3·20	......	7·52	5·92
„ sulphite, hyposulphite, polysulphides	......	......	......	......	3·78	......	......	......	......	......	......
Magnesium oxide	......	0·8	......	......	0·25	......	......	0·10	0·51	0·19	......
„ silicate	4·74	......	......	2·03	......	0·88	3·74	......	......	......	......
Silica	......	4·6	......	......	......	......	......	0·89	1·36	1·74	......
Earthy phosphates	......	......	......		2·66	......	......	......	......	......	......
Ferric oxide	......	......	3·02	6·23		......	......	1·75	2·40	1·48	1·21
Alumina	trace	1·2	1·02		1·13	......	......	0·79	......	0·72	......
Iron sulphide	2·45	1·2	......	......	0·37	1·22	4·92	......	......	......	......
Ultramarine	......	......	......	......	0·96	......	0·29	......	......	......	......
Sand	2·02	0·4	2·26	......	0·90	0·44	4·28	2·20	1·16	2·66	......
Coal	1·59	2·6	4·72	......	7·01	4·28	8·00	5·32	5·43	5·28	1·20
Water	2·10	......	......	0·99	0·22	2·17	0·52	......	6·71	......	......
Total	99·78	99·1	99·49	100·02	100·21	100·00	100·20	100·93	100·00	100·26	98·49

quoted in the table, a number of other but unimportant ones are found, coming partly from the brickwork of the furnaces. Of the cyanogen and ammonia compounds we have spoken previously; they have been very rarely estimated. Scheurer-Kestner, by treatment with alcohol, obtained from 100 grams black ash 0·073 gram. sodium sulphocyanide. In mother liquor from black ash Nietzki found 0·8 per cent. sodium ferrocyanide and 0·4 sodium sulphocyanide. The two latter are apparently formed during the dissolving, since cold alcohol only extracts sodium cyanide. The quantities of these compounds produced in the manufacture of soda, and hitherto not yielding any profit, but only doing harm, are not quite inconsiderable; Nietzki estimates them at 6½ tons of sodium ferrocyanide and 3½ tons of sodium sulphocyanide per annum for a daily make of 15 tons soda ash. Since the introduction of the Pechiney process the cyanides have been generally looked for, but they are usually estimated only in the black-ash solutions (tank-liquor).

Unger found the following rare substances in the black ash of Ringkuhl (analysis No. 1, p. 450):—

Titanium	0·151
Copper and molybdenum	0·025
Phosphorus	0·023
Tantalium	0·017
Fluorine	0·014
Barium	0·014
Nickel, cobalt	0·013
Manganese	0·013
Lead	0·013
Total ...	0·283

Further, in black ash there have been found selenium (by Scheurer-Kestner), arsenic (by Fresenius), vanadium (by Rammelsberg).

The following analyses by Davis (Chem. News, xxx. p. 176) are remarkable for the minute specialization of constituents for which exact analytical methods are not known; they have at any rate the merit of distinguishing between those soluble and those insoluble in water, and also of taking account of the insoluble soda.

Soluble:—

	a.	b.	c.
Sodium carbonate	28·144	31·807	28·336
" oxide	5·860	5·614	3·844
" chloride	2·808	2·574	3·101
" sulphate	0·192	0·190	3·037
" sulphite	0·151	0·072	......
" hyposulphite	0·189	0·853	0·126
" sulphide	0·358	0·163	6·645
" aluminate	0·344	0·752	0·923
" silicate	1·026	0·914	0·758
" cyanide	0·186	0·043	0·422
" sulphocyanide	0·074	0·021	0·077

Insoluble:—

	a.	b.	c.
Calcium sulphide	29·504	28·744	33·245
" carbonate	12·657	9·272	6·087
" oxide	10·048	9·488	3·465
Iron sulphide	0·554	0·774	1·355
Alumina	0·172	1·042	0·624
Silica	1·095	0·923	3·973
Magnesia	0·266	0·322	0·146
Sodium oxide	0·344	0·546	0·577
Carbon	4·263	4·483	4·958
Sand	1·237	0·875	0·842
	99·472	99·472	99·641
Soluble iron sulphide	......	......	0·105

a and *b* were good balls, *c* a burnt (red) ball.

Analyses of Balls made by the Pechiney-Weldon process.

	Black ash made with 60 per cent. mixing-coal.	Black ash made with 77·8 limestone and 36·1 coal to 100 sulphate.	Black ash made with 85·3 limestone and 44·1 coal to 100 sulphate.
Alkali	22·60 to 24·51	24·25 to 26·00	23·00 to 26·25
Na_2S	0·28 " 0·38	0·31 " 0·48	0·20 " 0·37
Na_2S to 100 alkali	1·15 " 1·60	......	......
Na_2SO_4	0·41 " 0·63	0·18 " 0·90	0·18 " 0·90
Total Na_2SO_4 after oxidation	1·85 " 2·24	0·88 " 1·90	0·96 " 2·00
Available alkali in the soda ash	57·40 " 58·30	......	......
Alkali in soda-waste	0·21 " 0·37	0·19 " 0·23	0·14 " 0·31
Na_4FeCy_6	......	traces " 0·06	traces " 0·052

If we neglect the caustic soda as such and add it to the carbonate, as, we have seen and shall see again, we are quite entitled to do, we find that black ash on the whole consists of 36 to 40 per cent. sodium carbonate and varying quantities of calcium sulphide, oxide, and carbonate. Besides, among the soluble constituents occur sodium chloride (due to the sulphate), and undecomposed sulphate (or sulphate re-formed by gypsum)—also cyanogen and sulphocyanogen compounds (due to the nitrogen of the coal), sodium aluminate and silicate (due to the coal-ashes and the brickwork), and sundry sulphur compounds of sodium with more or less oxygen (due to the action of calcium sulphide, along with that of atmospheric oxygen, during the lixiviation). The insoluble minor constituents mostly require no explanation. Ultramarine, as is well known, was discovered for the first time as an artificial compound in a black-ash furnace (Tessaert and Vauquelin); but only a few chemists indicate it. The "soluble iron sulphide" is present as ferro-sodium sulphide, which colours the black-ash solution yellow or even dark green; it occurs in sensible quantities in bad black ash only.

Behaviour of Black Ash in the Air.

Black ash, if exposed to the air under ordinary circumstances, soon exhibits a change. This subject has been frequently investigated most explicitly by Kolb (Ann. chim. phys. Juin 1866, p. 35). Of great importance in this respect are the *moisture* and *carbonic acid* of the air. If deprived of these two, air acts very little on black ash either cold or at 100° C.: its weight increases very little; and its composition is not very much altered. The black ash the analysis of which is stated in the table on p. 450, and which was made with special care, yielded on being dissolved (*a*, lixiviated at once; *b*, having lain for a month in the ground state in dry air free from CO_2, at the ordinary temperature; *c*, having been exposed for a month to a dry current of air in a place heated to 100° C.; *d*, having been heated to a red heat for four hours):—

	a. per cent.	*b.* per cent.	*c.* per cent.	*d.* per cent.
Increase of weight	...	0·40	0·31	8·6
Sodium carbonate	38·56	34·70	34·60	19·00
„ hydrate	3·30	5·70	5·70	5·10
„ sulphide	0·25	0·25	0·30	0·30
„ sulphate	0·92	...	...	24·30

Evidently the air at a high temperature, as Pelouze had previously found for temperatures beginning at 200° or 300° C. (Ann. chim. phys. lvi. p. 311), acts in such a way that CaS is converted into $CaSO_4$, which in the subsequent treatment with water is decomposed by Na_2CO_3, with formation of Na_2SO_4. The black ash ignited in the air is brownish white, owing to the coal being burnt and only the colour due to ferric oxide remaining. This shows that black ash ought not to be kept any longer than necessary in the air in a red-hot state. No doubt it would be best to let it cool in closed boxes; but this would be too troublesome, and is not done anywhere.

Dry carbon dioxide acts as little on black ash as on quicklime; but in a damp atmosphere of CO_2 the black ash *a* increased in weight by 32 grams, with considerable evolution of H_2S, and then yielded a lemon-coloured liquor containing:—

Na_2CO_3	32·50
Na_2O	0·00
Na_2S	6·05
Na_2S_2	4·12

Damp CO_2 consequently first converts the lime into carbonate, so that no NaOH is found; but then it evidently acts upon the calcium sulphide with formation of $CaCO_3$ and H_2S. A portion of the latter escapes in the gaseous state; another portion with CaS forms soluble $Ca(SH)_2$, which on lixiviation gives rise to the formation of Na_2S and Na_2S_2.

In the absence of CO_2, air saturated with moisture acts thus:—100 grams, exposed to it for a month at 15° C., weighed 157·40 grams; the solution contained

Na_2CO_3	28·70
Na_2O	6·92
Na_2S	0 30
Na_2SO_4	6·27
$Na_2S_2O_3$	traces.

Oxidation had evidently taken place, as on igniting; but in the latter case no hyposulphite can be formed, because it does not stand a red heat. According to Kolb, not much of it is formed from CaS,

because this at once changes into $CaSO_4$ (?), but from Na_2S, and consequently mostly from burnt balls, which contain much of the latter. Iron also may cause a diminution of the alkalimetrical test of black ash. This may contain up to 3 per cent. Fe, entirely as oxide, since iron sulphide and lime on ignition yield ferric oxide and calcium sulphide. But in the presence of water, first ferric hydroxide, and then, from this by CaS, FeS is formed, which in damp air is oxidized first to ferrous sulphate, then to basic ferric sulphate; and the latter with lime and calcium sulphide again yields $Fe_2(OH)_6$ and FeS, which again play the same part as before. Thus a small quantity of iron may ultimately convert all CaS into $CaSO_4$ [but only in very favourable circumstances, such as never occur in practice].

The above experiments of Kolb (and others) fully explain the facts observed in practice. When black ash is exposed to moist air, first the lime is hydrated; the increase of volume accompanying this produces cracks in the balls, so that they fall asunder. The fragments, if exposed to the air for a longer time, divide again into smaller pieces, and at last are reduced to powder. This point they ought not to be allowed to reach; for whatever may be gained by the lime being carbonated and thus producing less caustic soda, is far more than counterbalanced by the disadvantage arising from the above-described oxidation of calcium sulphide. The balls ought to be left only till they have sufficiently cooled down to be conveniently broken and handled: in that case a portion of the lime will be slaked; and this will facilitate the breaking of the balls. For this 24 hours after drawing is hardly sufficient; but two days are enough, and more time should not elapse (although Kolb allows from three to six days), because the heat still remaining in the balls materially assists their lixiviation.

The author ought to state here that he was assured at a large and well-managed German works, producing an excellent quality and very strong alkali, that they ascribed this to their allowing the balls to lie for two or three weeks before dissolving them. He cannot, it is true, vouch for the accuracy of this; but it should be mentioned that there the balls were not, as usual, lying on an open ball-bank, but stowed away in a close, box-like place, where the air had very little access to them. This must take much manual labour.

On keeping for a long time in ordinary air, containing moisture and CO_2, black ash is constantly undergoing change, whereby it is deteriorated. In a sample which originally contained, as was ascertained by testing, 29 per cent. of sodium carbonate, Erdmann (Wagner's Jahresb. 1860, p. 181) found, after 27 years' keeping, mere traces of that salt.

The Action of Water upon Black Ash,

one of the most important questions in alkali-making, has also been carefully investigated by Kolb (*loc. cit.*). That no *caustic soda* occurs as such in black ash, is proved by its not yielding any to alcohol, even after moistening it previously in order to convert Na_2O into NaOH (Pelouze and Unger). Kynaston and Scheurer-Kestner had shown the same thing, and proved that its presence in tank-liquors is only owing to the action of lime upon Na_2CO_3. Kolb proved this further by obtaining the most varying quantities of caustic from the same black ash, by varying the quantity of water, its temperature, and the duration of the treatment. This holds good still more of *sodium sulphide*, of which in good black ash only traces occur; but on treating the black ash with water, according to the differences of treatment, very different quantities appear. Usually only monosulphide can be met with, because in the presence of caustic the polysulphides must be converted into monosulphide.

In order to study the action of water on black ash, Kolb employed the black ash mentioned on p. 453, and used in his other experiments, of which he always treated 100 grams,—1st, with varying quantities of water (350, 500, 1000, and 2000 c. c.); 2ndly, for varying times (6 hours, 24 hours, a week); 3rdly, at different temperatures (15°, 40°, and 60° C.). He then estimated the percentage of Na_2CO_3 in the liquid and the caustic and sodium sulphide formed by the action of CaO and CaS. His results were as follows :—

100 grams black ash treated with	Cub. centims. of water.	For 6 hours, at			For 24 hours, at			For a week, at		
		15°.	40°.	60°.	15°.	40°.	60°.	15°.	40°.	60°.
	350									
Na_2CO_3		...	...	...	34·7	31·4	31·5	31·5	25·8	26·4
Na_2O		...	...	...	5·7	7·8	7·6	7·6	9·5	7·2
Na_2S		...	...	...	trace.	0·2	0·3	trace.	2·2	3·7
	500									
Na_2CO_3		38·5	37·4	31·5	38·6	35·4	26·8	37·0	34·2	25·5
Na_2O		3·3	3·9	6·8	3·3	5·1	6·7	4·2	5·7	6·6
Na_2S		0·2	0·3	0·7	0·3	0·4	4·7	0·3	0·4	5·9
	1000									
Na_2CO_3		40·2	35·9	34·2	38·6	34·2	31·1	35·2	31·4	23·2
Na_2O		2·3	4·4	5·4	3·3	6·0	6·6	5·0	6·3	6·0
Na_2S		0·3	0·5	0·8	0·3	0·8	2·0	0·3	0·8	7·8
	2000									
Na_2CO_3		38·2	36·1	37·9	37·6	34·7	33·1	34·5	31·5	19·5
Na_2O		3·3	4·7	3·3	3·8	5·9	6·2	5·3	6·3	6·3
Na_2S		0·2	0·5	0·6	0·4	0·5	1·0	0·5	1·5	10·2

From this the following conclusions can be drawn:—1st. The *causticity* is not materially influenced by the quantity of water, but increases both with the time of digestion and the rise of temperature. This is not surprising, since from the outset enough water is present to complete the reaction. 2nd. The *sodium sulphide* is also increased very little with an increase of the quantity of water, but very much by increasing the time of digestion and raising the temperature. 3rd. The quantities of caustic and sulphide formed have no relation to each other; the decrease in sodium carbonate coincides not only with the formation of caustic, but also with that of sulphide; the latter consequently seems to be formed from the carbonate, not from the caustic.

In order to discover more exactly the reactions producing sulphides in the liquor, Kolb made experiments on the action of water on CaS by itself, and in the presence of sodium carbonate, caustic, and lime, partly by themselves, partly associated.

One litre of water dissolved in 48 hours:—At

10°	18°,	40°,	60°,	90°,	after 2 hours' boiling,
0·15	0·23	0·30	0·48	0·33	0·27 gram CaS.

[Gossage (Chem. News, vi. p. 269) calls CaS "insoluble" in water; Scheurer-Kestner (Compt. Rend. lvii. p. 1013) found that at 12°·6 C. 1 part of CaS was soluble in 12,500 parts of water.]

Sodium chloride makes CaS less soluble; on adding 5 grams NaCl, 1 litre of water dissolved, at

10°,	40°,	60°,
0·07	0·18	0·42 gram CaS.

Sodium sulphate very slightly increases the solubility of CaS. *Lime-water* makes no perceptible difference. In any case CaS enters into solution as sulphhydrate:

$$2CaS + 2H_2O = Ca(SH)_2 + Ca(OH)_2.$$

This conversion takes place very slowly, even when CaS is boiled with water. By itself the presence of lime has no effect upon it; but it has an effect if sodium carbonate is present as well. A solution of *caustic soda* (3·15 gram Na_2O per litre), both at 10° and 100° C., takes up mere traces of sulphur from CaS; equally so solutions containing 16·7, 42, or 79 grams Na_2O per litre. But if these stronger solutions are digested with CaS *for a longer period,*

say 48 hours, at temperatures varying from 40° to 100° C., the reaction $CaS + 2NaOH = Ca(OH)_2 + Na_2S$ takes place all the more completely the more concentrated the solutions are. Inversely Na_2S is *not* changed by quicklime.

A saturated solution of *sodium carbonate* has next to no action on CaS; but the decomposition increases with its dilution as well as with a rise of temperature and the time of digestion; it is greatly retarded by the presence of caustic soda, as well as by that of lime, which produces caustic.

The following table shows the particulars:—

CaS in excess treated with 1 litre of an aqueous solution containing			Of 100 parts Na_2CO_3 there have vanished by conversion into Na_2S after a time of digestion of		
Na_2Co_3.	Na_2O.	CaO.	6 hours at 15° C.	48 hours at 15° C.	48 hours at 60° C.
grams.	grams.	grams.			
37	...	...	4·75	21·5	32·5
37	...	5	1·19	9·2	22·4
80	...	...	1·25	6·1	17·0
80	...	5	0·71	1·3	14·0
80	5	...	0·68	1·1	11·2
130	...	...	0·51	2·4	3·2 *
130	...	10	traces.	0·9	3·1 *
285	...	...	0·20	1·8	4·8
285	10	...	traces.	1·1	3·4
285	...	10	traces.	0·9	3·1

From his investigations on the action of water upon black ash and each of its constituents, Kolb concludes that, in order to get the smallest possible quantity of caustic and sulphide into the liquors, the black ash ought to be lixiviated as quickly as possible, with the smallest possible quantity of water, and at the lowest possible temperature; it would be best if an apparatus could be invented by means of which black ash could be lixiviated cold within a few hours, and at the same time a concentrated liquor were obtained, which would then be almost free from sulphide. This was known

* After 2 hours' boiling.

to practical men before Kolb; but the accomplishment of his desiderata is almost chimerical, since opposite things are required, viz. *cold* lixiviation along with *speed* and with *concentration* of the liquor.

Pelouze (Compt. Rend. lxii. p. 315) has made an investigation similar to Kolb's; but his paper adds nothing of importance to Kolb's labours, and is of greater importance only as an argument against the calcium-oxysulphide theory.

Lixiviation of Black Ash.

In the childhood of soda-making the black ash was sent into the trade just as it came from the furnace, and was chiefly bought by the soap-makers. In Marseilles especially it was made on a large scale for this purpose, and was imported thence into London in that form up to 1818 (Mactear, Report on the Alkali, &c., in the Glasgow District, p. 26). In England it was known as "British barilla," and usually contained 10 or 12 per cent. common salt, which of course mostly did no harm to the soap. From what we have just now seen, this artificial "barilla" could not but deteriorate continually on being kept, even in casks; the formation of sulphide would not do so very much harm, because that would still saponify the fat; but the sulphate was a dead loss. Glass also, of course only green or black, was made with black ash.

For good reasons, black ash has long since gone out almost entirely as a commercial product, being still sold only in a few places in France to neighbouring soap-works. It is always submitted to the process of *lixiviation*, by which the soluble constituents are separated from the insoluble—partly in order to obtain a purer article, partly to prevent both the re-formation of sulphate from the carbonate and other injurious effects of the calcium sulphide. Lixiviating appears to be a very simple affair; but in fact even the mechanical portion has only recently been perfected so as to obtain a concentrated solution at little cost; and the process altogether is far from being a merely mechanical one, since the injurious chemical changes in the mass are favoured by precisely the same circumstances which are favourable to good lixiviation, viz. a high temperature and a long period of digestion. Consequently the management of the lixiviation requires great care and an intel-

ligent and attentive workman, lest even perfectly good black ash yield bad liquor.

Even with the best will and all exertions, the lixiviation on the large scale cannot be conducted without some sulphate being re-formed. With very good work in hand-furnaces only 1 per cent. of the sulphate remains undecomposed, and even much less in revolving furnaces; but in the liquors as they are obtained on the large scale, in the majority of works 3 or 4 per cent. sulphate (calculated on the salt) is found, and frequently twice as much if any of the precautions to be mentioned are neglected. In what way the sulphate is formed in this case we have already seen; the black ash being exposed to the air, and especially to moist air, has most to do with its alteration.

Neither can the formation of sodium sulphide be entirely avoided; it can only be kept within bounds by using all care, especially by quick and not too hot washing. Usually the formation of caustic soda occurs at the same time, especially in dilute liquors, in which soda is more readily causticized by lime.

In the modern system of lixiviation the black ash is required in rough pieces, and only broken up sufficiently for easy handling; the crushing-rolls or pounding-mills formerly in use for it have vanished. If the black ash is porous enough, about which we have seen before, the lixiviating liquid penetrates the mass much more easily in the rough than in the ground state. On the other hand, it is essential that the pieces be firm enough to keep their form for some time during lixiviation, at least till the whole mass is quite uniformly penetrated with liquor. The demand made in some treatises, that it should keep its shape to the end of the lixiviation, is impossible to fulfil; at that time the mass has settled down to three fifths or one half of the original bulk. On the contrary, good black ash will always go down so far, whilst non-porous black ash, either "soft" (*i. e.* drawn too soon) or burnt (*i. e.* drawn too late), does not go down in the tanks, because it cannot be properly lixiviated. Black ash made with limestone is not so easily lixiviated as that made with chalk, and mostly cannot be exhausted to the same extent.

Well-made black ash, drawn in the proper state of pasty fusion, is honeycombed by the gas-bubbles escaping, analogous to a fermenting loaf of bread, because the gas cannot escape immediately, owing to the toughness of the mass—and thus is in an

excellent state for lixiviating. It is only necessary to wait for 48 hours, when the mass will be cool enough for handling (see p. 455); it is then broken up with heavy hammers into pieces of the size of a child's head; of course, among these, smaller pieces are also obtained. On the Continent it is sometimes found necessary to crush or grind the black ash if the furnaces do not go hot enough and consequently "soft" balls are obtained, or from the large furnaces, in which they are easily overheated—also those made with much less coal than in England. In this country not even revolver-balls are crushed, but only broken by hand.

Such dense balls, as they are obtained by heating too little or too much, even after prolonged contact with water leave an unchanged core if employed in large pieces. It is well known that calcined soda thrown into water is converted into a stony hard mass which resists dissolving for a long time; the same takes place with black ash if presented to the water in hard lumps.

Where the black ash has to be crushed (for instance, that from the large French furnaces), it is reduced to pieces of the size of a walnut, mostly by means of two rollers studded all over with blunt steel teeth of the shape of a truncated pyramid at distances of $\frac{3}{4}$ to 1 inch; the distance between the teeth of the two rollers is $\frac{1}{2}$ inch. The rollers are so arranged that they stop if too large or too hard a lump gets between them. The black ash falls from a hopper onto the rollers, and, after crushing, onto an oscillating sieve, where the powder is riddled off; the latter is spread very equally all over the small pieces, so that these act as a filter and do not allow the powder to be washed away.

The first requirement in lixiviating is, of course, to *completely* exhaust the black ash and at the same time to obtain as *concentrated* a liquor as possible, so as to save expense in boiling-down; and this at the same time fulfils one of the requirements previously stated as necessary for proper lixiviation. But this, in order not to damage the chemical composition of the liquor, must be combined with *quick work* and *a moderate temperature.* Experience has shown that pretty *concentrated* liquor may be left in contact with black ash at 60° C. without any danger; but *weak liquor* or *fresh water* acts injuriously on partially exhausted black ash at a much lower temperature, forming much sulphide; here even in winter 43° (better only 37°), in summer 32° C. ought not to be exceeded.

The lixiviating process must invariably be accommodated to this rule.

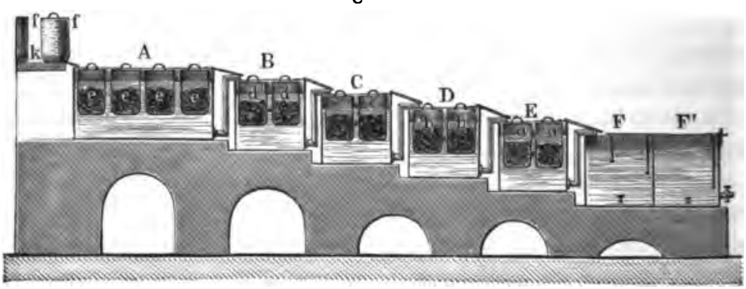
A very important distinction in the kind of lixiviation is founded upon whether it takes place with the *mass at rest* and the liquid circulating, or with the *mass circulating*. Not merely is the construction of apparatus quite different in the two cases, but also the result. With the mass at rest, *i. e.* if the black ash always remains in the same vessel, the water or liquor passing through it, the mass remains open and porous for a much longer time, and thus acts itself as a kind of filter, so that much clearer liquors are obtained than if the mass is moved by transferring it to another vessel: in the latter case it soon settles down to a very dense and not easily permeable mud, which makes the labour of lixiviation much more difficult and requires much larger quantities of water for exhaustion.

The oldest apparatus for lixiviation, such as is hardly anywhere employed now, consisted of three rows of iron tanks, placed terrace-fashion one above the other, each of them provided with an outlet-cock a little above the bottom. Fresh water was run into the top tier, the weak liquor from this into the second and then into the third tier, from which the finished liquor was run off at the bottom. Inversely, the black ash was first put into the bottom tanks, where it only reached up to the level of the cocks; after the liquor from the second tier had become quite saturated by that fresh black ash, the same, now partly exhausted, was shovelled up into the middle tanks, then just in the same way into the top tanks, and at last onto the waste-heap. Here usually the fresh water was not heated; only the last liquor was heated by the black ash charged in the hot state: and it cannot be denied that this was right; but this method, apparently right in principle, was rendered very imperfect in operation by the transferring of the mass involving a great deal of labour, by the dense settling-down of the same, by its merely superficial contact with the liquid, and that always with its strongest portion, and by the muddy state of the liquor, which could never be made very strong and always contained much sulphide.

Much more perfect was the apparatus introduced by Clément-Desormes, founded upon the well-known principle that any soluble substance, such as salt, sugar, &c., dissolves in water much more quickly if placed just below its surface, than if placed on the bottom of the vessel. In the latter case it is soon covered by a concen-

trated solution, preventing its contact with the water higher up, and only very gradually exchanging its contents with the latter by diffusion, unless agitated. In the former case the solution formed at once sinks down, so that fresh water constantly gets at the soluble body. Upon this principle Clément-Desormes placed the black ash in perforated vessels just below the level of the liquid, and also in other respects arranged the apparatus for methodical lixiviation. It is shown in fig. 192. The roughly crushed black ash is put into

Fig. 192.



sieves *a a* to *e e*, made of perforated sheet iron, provided with loops at the top, and hung upon an iron rod passed through these in the lixiviating tanks A to E, so that they dip below the level of the liquid. Usually two, sometimes even four sieves hang in one of the tanks A to E. These tanks are mostly placed two on the same level, and in from 5 to 12 tiers, each a little higher than the next. The fresh water enters first into the top tank A; from this it runs into the next lower tank B by means of an overflow-pipe, so that the liquid from the bottom of A runs in at the top of B; and thus it passes through all the tiers till the concentrated liquor at last runs into the settlers F F'. In this way the liquors of different strengths are not mixed, but the strength continuously increases throughout the whole set. On the other hand the sieves *a a* to *e e*, filled with black ash, are first put into the bottom tank E, after some time into the next higher tank D, and so forth; after the last sieves have been in contact with fresh water, they are allowed to drain (*f*); and then their contents are put on the waste-heap. Here, also, the strong liquor meets fresh black ash, the fresh water nearly exhausted ash, and the soluble portions are gradually extracted in a methodical way. The transferring of the sieves is

facilitated by a travelling pulley or winch, which can be placed over each tank. A steam-pipe runs alongside the tiers of tanks; these are heated gradually, more so as the liquor descends and becomes more concentrated. Each sieve holds from ½ to 1 cwt. of black ash; and for each ton of black ash to be lixiviated in 24 hours 40 or 50 such sieves are required. Mostly the sieves are left 25 or 30 minutes in each tank before being transferred to the next higher one; with 15 sieves it thus takes eight hours before a sieve has arrived at the top. Here it is allowed to drain on an inclined plane; it is then replaced by another, and so forth. Each time that a sieve full of fresh black ash is put in, about twice the same volume of water is run in at the top. There must be a series of settlers, because the liquors are very muddy.

Clément-Desormes's system was soon generally introduced in France and Germany, and was there given up, for the much simpler and better method now in use, only since 1862, when the latter, erroneously called Shanks's plan, became more generally known by Hofmann's Report by the Juries on the International Exhibition. The former system furnishes concentrated liquors and completely exhausts the black ash; but, owing to the frequent moving about of the sieves, the sediment settles down into a very dense mass, especially when the sieves have been lifted out of the tanks and the particles of the mass are no longer partially supported by immersion in liquid; from this very muddy liquors result, and the lixiviation is much retarded, compelling frequent repetition of the treatment and multiplication of apparatus, and finally producing bad liquors. The worst is the great amount of labour for the constant changing of the sieves and the frequent cleaning and boring-out of the holes. For 3½ tons of black ash per diem, *e.g.*, 160 or 170 sieves and 8 men (4 by day and 4 by night) are required. A single English ball-furnace would require 300 sieves. Clément's apparatus also takes up much room. This kind of lixiviation requires denser black ash, less liable to fall to powder; it must be made with less coal, and owes to this a much lighter, often yellow colour, along with great hardness.

It is remarkable that the modern style of lixiviation, now to be described, has taken so much time for its general introduction, in spite of its being the cheapest to erect and the simplest, most rational, and perfect to work. It was usual to call it Shanks's lixiviating process, after A. W. Hofmann, in his Report by the Juries,

p. 22, upon the authority of Mr. Gossage, had unconditionally claimed the honour of its invention for the late Mr. James Shanks of St. Helens. Muspratt had previously asserted (in his Dictionary, ii. p. 926) that "he knows it as a foreign invention which was introduced by Mr. C. T. Dunlop into the St.-Rollox Chemical Works about the year 1843;" but Hofmann's statement was almost universally credited. This cannot be done now, since Scheurer-Kestner (in the 'Bulletin de la Société industrielle de Mulhouse,' Feb. 28th, 1868) has completely elucidated the matter, and proved Muspratt's statement to be substantially correct. He reports that in October 1856 he had visited Messrs. Tennants' works on a journey to Scotland, in company with Mr. Gundelach, of Mannheim. Mr. Dunlop then showed to them the apparatus working by displacement of the liquor, *just in the same form as to-day*, and stated to them that it had been at work for more than ten years (this agrees with Muspratt's year, 1843); moreover Mr. Dunlop told them that he had constructed the apparatus in consequence of advice given him by Mr. Gundelach on a previous visit. Mr. Gundelach himself now informed Mr. Scheurer-Kestner that the original idea had been given to him by the well-known physicist, Professor Buff of Giessen, who a few years before had made a few experiments with it at Kestner's works at Thann, to which no further development was given; on the strength of these Mr. Gundelach had given that advice to Mr. Dunlop. After this testimony of Scheurer-Kestner, founded on direct personal inspection and oral evidence, it is not possible to doubt that the present generally practised methodical plan of lixiviating was first proposed by Buff, and practically carried out by Dunlop, probably many years before Shanks had introduced it in Lancashire, possibly independently, although it is difficult to suppose that he had never seen or heard of the St.-Rollox plant.

In any case it is singular that the Buff-Dunlop apparatus, which about 1860 was probably the only one employed in England, has made its way abroad so very slowly. Scheurer-Kestner introduced it at Thann soon after his return, in 1858; but he was not followed by the other French alkali-makers. In the *last* edition of Payen's 'Précis de Chimie industrielle' (1877), the Clément-Desormes apparatus is described at length, whilst to that cited as Shanks's apparatus only eight lines are given. In Belgium, in 1864, according to Chandelon, none but Clément's apparatus was in

existence. In Germany Gundelach introduced the Buff-Dunlop plan in 1858, at the Mannheim works, but apparently had no successors till, in 1865, Schaffner introduced it at Aussig; and not till after that date was it generally adopted in Germany and Austria. The last apparatus of Clément's in Germany was only abandoned in 1877, and in France probably about the same time.

The Buff-Dunlop lixiviating system retains from Clément's the disposition of the mass as nearly as possible just below the level of the liquid, also the methodical meeting of fresh mass with almost concentrated liquor and of nearly exhausted mass with fresh water; but it adds a principle of decisive importance, viz. that of allowing the mass to rest in the same place till it has been completely exhausted, and causing only the liquid to circulate so as to be gradually increased in strength as it comes into contact with the black ash in the inverse order. By allowing the black ash to remain always in the same place till it is completely exhausted, when it is cast out and put on the waste-heap, its porosity is retained much longer; and even after the pieces have long lost their shape and have been turned into a more or less coarse powder, the latter never settles down so densely as in Clément's sieves, because it always remains submerged in the liquid, and a portion of its weight is consequently supported by the latter. For this reason alone a much smaller number of tanks and much less time suffice for the lixiviation; and there is an enormous saving of labour, as will be clear without any explanation. One man by day and one by night can lixiviate the make of five or six black-ash furnaces, *i. e.* from 30 to 36 tons of black ash—of course without filling and casting out the mass, which takes about one man per furnace. Another very important advantage of never allowing the black ash to emerge from the liquid is this—that no moist calcium sulphide is oxidized to sulphate by the atmospheric oxygen, which would cause a loss of soda.

According to Chandelon (Monit. Scient. 1864, p. 52), the expense of lixiviation by Clément's apparatus in 1864 amounted to 5 francs per ton of black ash, against 72 centimes with Shanks's system in England, in spite of the higher rate of wages paid there.

The principle that the mass should remain at rest involved another. It was no longer possible, as in all previous systems of lixiviation, to cause the locomotion of the liquors by a difference in the level of the tanks; for since all the tanks are filled with

the same fresh balls, they must all be placed at the same level and each tank must pass through all stages of lixiviation—that is, serve as first, second, and last for the admission of water; there must be a true system of circulation. This might be attained by pumping the liquor from the bottom of one vessel to the top of another. This is actually done in some cases, *e. g.* in wet copper-extraction, in Schützenbach's beet-sugar maceration process, &c., by means of injectors, centrifugal pumps, &c. In the soda-manufacture, however, and, following its example, in many other cases, the circulation of the liquid is caused without any mechanical assistance, simply by its hydrostatical pressure. Singularly enough, this matter, extremely simple as it is, is wrongly explained in Hofmann's Report by the Juries, p. 23. There the principle of the liquor-motion is reduced to the fact that solutions become heavier as they become richer, and that any given column of a weak solution is balanced by a shorter column of a dense one. Hence, in a series of horizontally disposed lixiviating vats the water-level will be lower in each successive vat, viz. highest in that receiving pure water, lowest in that containing saturated liquor. Thus, though the vats themselves be horizontal, a "working declivity" of from 12 to 15 inches is stated to be gained. Now a declivity of course exists, but not a "working" one; the liquor cannot flow from the weaker tanks to the stronger ones, although their level may be very different, if this difference is only caused by that in the specific gravities of the solutions. According to the law of communicating tubes, the liquid cannot run out of the stronger limb (or tank) unless the level of the liquid in the weaker limb is still *higher* than corresponds to their relative densities. Hence in vessels of equal height and placed at the same level the principle cited by Hofmann could only be employed for forcing the liquid from the stronger to the weaker vessel, because at equal height there is a pressure from the stronger towards the weaker limb. But since just the contrary is needed, viz. a current from the weak tank towards the strong one, and since in the connecting tubes &c. a certain amount of friction has to be overcome by a corresponding pressure, the tanks must be made higher and those openings from which the strong liquor issues must be made low enough to satisfy not merely the difference of level between the water and the strong liquor, but also the pressure required for overcoming the friction. The head of water between the top of the tank and the lateral exit-

opening is the real moving principle; if it is made too low, or if by a partial obstruction of the connecting-pipes the friction is increased, the weak tank will run over before the strong one begins to run. This latter accordingly runs not because, but although the level of the liquid in it is lower than in the weak tank.

Sometimes the strong liquor is not run off sideways, but by the bottom cock; this is the case in nearly all published diagrams, and on the Continent is usually found in practice as well. This arrangement, as is easily seen, has nothing to do with the explanation given by Hofmann; here also the principle of communicating tubes is the only one employed. But it has this drawback, that the outlet-cock must be regulated exactly to suit the inlet-cock; and this must be repeated for each change of either one or the other, lest either the last tank get empty or the first one run over. If, as shown in the following description at *ff*, separate run-off pipes are provided, starting from the bottom and ending laterally, nothing else need be done than regulating the inlet into the first or "weak" tank, and at the same time as much descent is gained for the liquor as corresponds to the difference of level between the bottom cock and the lateral outflow.

In figs. 193 to 195 a set of lixiviating tanks (or vats, as they are usually called in Lancashire), such as is actually used in practice, is shown on scales of $\frac{1}{50}$ and $\frac{1}{36}$.

We show four tanks; this is the minimum number, and at the same time that mostly met with; rarely are there upwards of six tanks in a set, unless the lixiviation is combined with Mond's sulphur-recovery process (see Chap. XIV.). Usually the tanks are, as drawn here, not separate, but formed of a long tank divided into compartments by partitions. Each of these tanks, $7 \times 7 \times 5$ feet, holds 20 or at most 24 balls of 3 cwt. each of sulphate. As from one charge to the other 48 hours must be reckoned, this set can at most accommodate the make of two ball-furnaces yielding 24 balls per diem. In large works the tanks are mostly made much larger: those of $10 \times 10 \times 6$ feet hold 48 or 50 balls; and five of them can serve as many ball-furnaces. It is advisable in any case to have a certain excess of lixiviating-space, and not to hurry the "casting" too much; otherwise the waste will be often found to be incompletely washed.

Very commonly the tanks are placed on the ground-level, partly on account of their weight, partly to save hoisting up the black

Fig. 193.

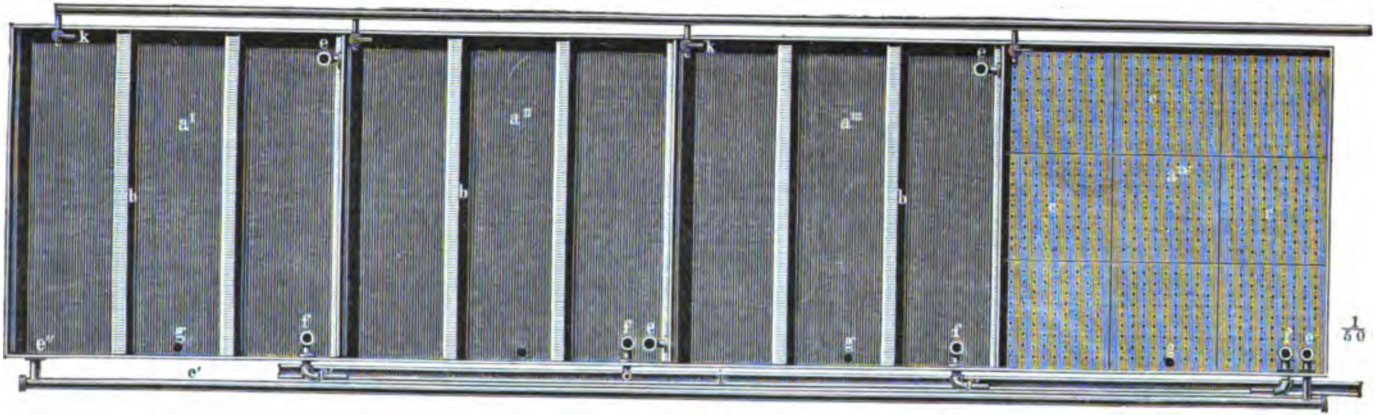


Fig. 194.

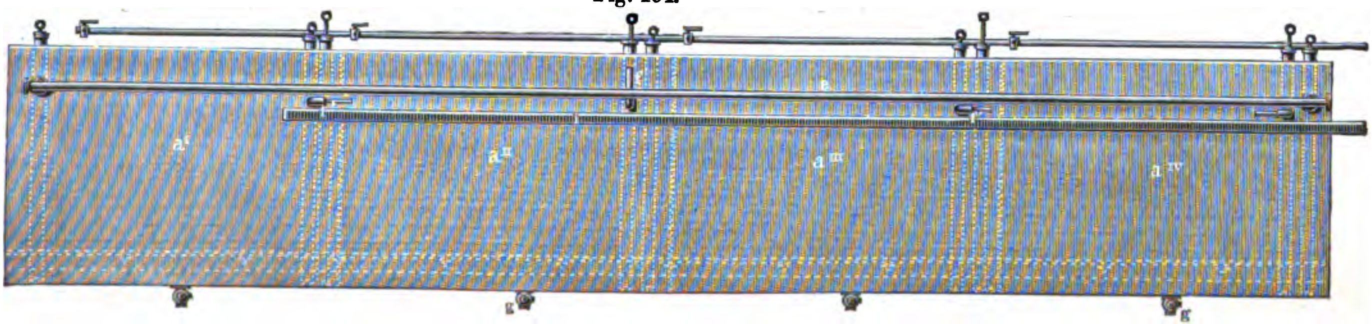


Fig. 195.

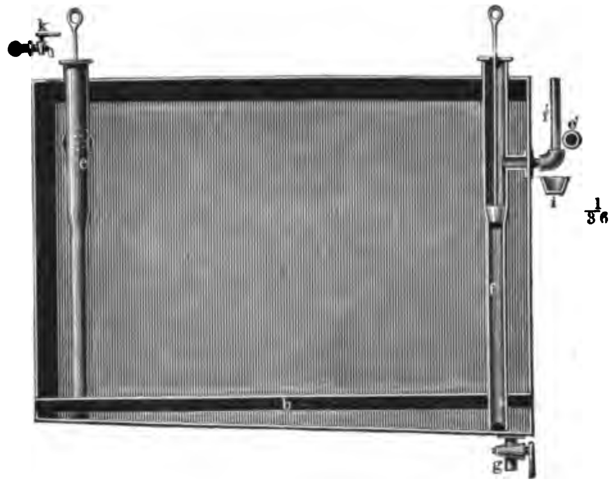
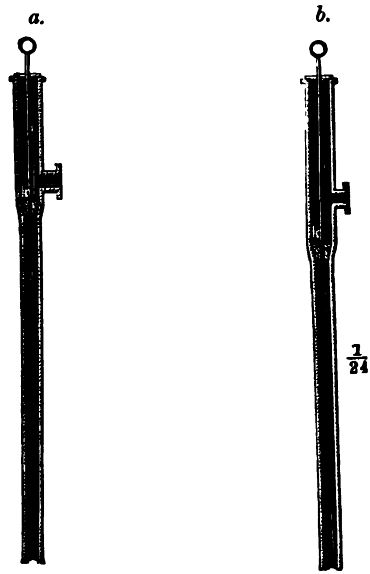


Fig. 196.



ash, which would take much more time than pumping the liquors. Sometimes they are even found sunk in the ground, which certainly keeps them very warm in winter. But a higher situation has the advantage that any leaks can be easily discovered and that the waste can be got out more conveniently. The special requirements of each factory will have to decide here. In any case the tanks should rest upon pillars of such height that they can be examined for leaks from time to time.

The tanks are fitted up as follows:—They are made of $\frac{5}{16}$- to $\frac{3}{8}$-inch boiler-plate, with their edge stiffened by an angle-iron or something like it; very large tanks are further protected against bulging of their sides by iron stays, bent down at the ends and dropped into loops riveted to the tank-sides. Near the bottom of each tank the T-irons *b b* are riveted on; their upper flat portion is 3 inches wide and 6 inches distant from the tank-bottom; they serve for supporting the false-bottom plates *c c*. If the tank-bottom is made to slope forward, the T-irons, which must be quite horizontal, at the back end are only 3 inches above the bottom. Along the two sides angle-irons *b′ b′* run, likewise as a support for the perforated plates. Formerly in lieu of perforated wrought-iron plates cast-iron ones were used; but these have been mostly abolished, because they are quickly broken and spoilt, whilst wrought-iron plates stand very well. The plates are cut to suit the size of the tank,—not too large, so as to be easily handled, as they have to be taken out every time on emptying a tank. They are about $\frac{3}{8}$ inch thick, and contain holes $\frac{1}{4}$ inch in diameter, and 3 to 4 inches from centre to centre.

Each of the tanks contains two overflow pipes (not one as in the published drawings), one of which serves for weak liquor, the other for running off the strong liquor. The former are in fig. 193 marked by *e e*; and in fig. 196, *a* shows one on an enlarged scale; the latter are marked *f f*, and in fig. 196 *b* shown separately. They are only distinguished by the position of the plug, which is lower in the second kind. They are cast-iron pipes, about 4 inches wide, a little wider in the upper part; the place where the pipe widens out is conically bored out; and in this place a conical plug *k* closes the pipe. The joint is either made tight simply by the plug being turned in the lathe and ground into the seat, or a groove is turned round the plug, into which tarred spun yarn is put; the former is preferable. Above the plug-seat the pipe has a side branch, which

is bolted to one side of the tank, perforated to suit. The whole pipe passes through a hole in one of the sieve-plates *c*, and stands on the tank-bottom; the liquor can enter into it through nicks cut in its lower end. If the plug *k* of the pipes *e e* is taken out, the tank, say a^{I}, communicates with a^{II}; the liquor rises from underneath the false bottom of a^{I} in the pipe *e* and overflows higher up into a^{II}. In the same way a^{II} is connected with a^{III}, and a^{III} with a^{IV}; but as each tank has to be alternately first, middle, and last, even a^{IV} must serve as first, a^{I} as second, and a^{II} as third, which is brought about by the side branch of the overflow in a^{IV} continuing into the pipe e', running the whole length of the tanks and at e'' again entering into a^{I}. In this way the contents of each tank may flow over into the next one. With the depth of tanks indicated here the centre of the side branch of *e e* must be about 4 feet above the tank-bottom.

The function of the pipes *f f* is this. Suppose a^{I} to be the first and a^{III} to be the last tank working—that is, fresh water running into a^{I}; the liquor, when tank a^{III} has run full, having penetrated through fresh balls, will be strong enough for running off. Already before this the communication between a^{III} and a^{IV} has been interrupted by putting the plug into *e*; now the pipe *f* begins to act, its plug having been taken out, whilst in the other tanks the plugs of *f* remain closed. The strong liquor now runs out of the side branch of *f*, the centre of which is 2 or 3 inches below that of the side branches of *e*. All the running-out pipes *f* for strong liquor are attached to the front of the boxes; into their outer opening a 2-inch gas-tube is fitted, bearing a screw-thread on its front end, round which an elbow and a short piece of pipe f' turns without difficulty. When the piece f' points upwards, *e.g.* in a^{I} and a^{II}, nothing can run out, even when the plug is open; but as soon as f' is turned into a horizontal position or even lower, the contents of the tank will run out as far as the level of the side branch; and if in a^{I} the supply of fresh water is continued, a corresponding quantity of liquor must continually run out of a^{III} through f'.

At some works, instead of the turning elbows at f', there are large cocks; but these are quite unnecessary, are easily stopped up by crystallization, and are much less convenient than the arrangement just described. The plugs *h* in the pipes *f* might even be dispensed with altogether, since the latter can only run out when f' is turned down; but the plugs are preferable, because the pipes are more

safely closed and crystallization in the pipes when they are out of use is avoided.

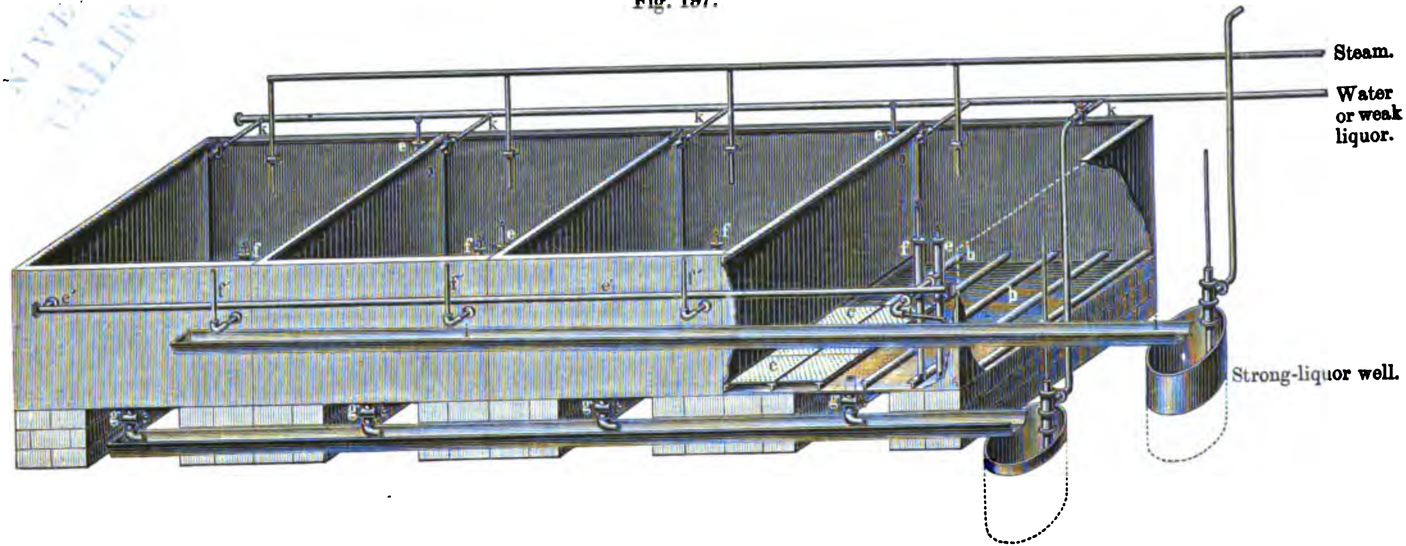
In the drawing an open shoot *i* is seen just underneath the side pipes *ff'*, so that these must empty into it; it leads to a well, in which the strong liquor is collected and afterwards pumped up or otherwise disposed of. In the place of this open shoot many works have a second cast-iron pipe, with which all the side branches of *ff* are connected by outside branches, and which ends in the well. The small pipes *f' f'* cannot be employed here; nor can the liquor running out be freely seen; but a sample can always be taken through *f*. The closed pipe very easily crystallizes up, and has no object, as it is not necessary here to keep it horizontal; hence an open shoot is altogether preferable. Even the pipe *e'* in winter quickly crystallizes up, and is therefore best lapped with straw; if steam is near by, a ½- or ¾-inch pipe is put into one of the ends of *e'*, in order to melt any crystals obstructing the pipe.

Each of the tanks a^{I} to a^{IV} is provided with a bottom-cock *g* of about 3 inches bore; it is advisable to make the bottom sloping towards the cock, so that the contents of the tank can all run away. In the case of Mond's sulphur-recovery process, where soda-liquor and sulphur-liquor are made in the same tank, a sloping bottom is indispensable.

Each of the tanks must have a supply of water; but the same water-pipe and cock may serve for two tanks if the branch pipe be laid over the partition between them; by means of a swivel-pipe and a small movable shoot the water can be run at will into either of the tanks. Besides these cold-water pipes, there must be either hot-water or steam pipes, according to the style of heating preferred; and a third set of pipes is required for the weakest liquor, which at the end of the lixiviation covers the exhausted residue: for this a single pipe can serve, and the liquid be conducted from it into any of the tanks by an india-rubber hose or by a shoot.

Instead of a completely fitted-up set of lixiviating-tanks such as are represented here and are now found in most works, even large works formerly had less perfect apparatus, especially so far as the false bottom is concerned. Some, *e. g.*, had the bottom laid with bricks, leaving cross gutters which were covered with sheet iron, &c. Others had no false bottom at all, but only a sieve round the overflow pipes standing in a corner. It is evident that thus no such regular action could be attained as with a perfect apparatus.

Fig. 197.



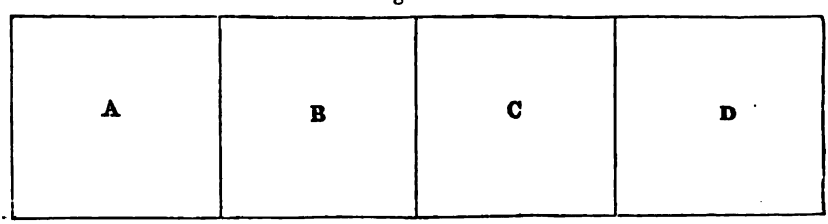
Steam.
Water or weak liquor.
Strong-liquor well.
Weak-liquor well.

Sometimes the tanks are surrounded by bad conductors of heat, which certainly seems to be advantageous.

Fig. 197 shows a larger, complete lixiviating apparatus, on a scale of 1 : 96, in isometrical projection, with part of the sides removed; it suffices for 50 balls of 3 cwt. sulphate in each tank. The letters have the same meaning as in the preceding figures.

The lixiviating process is carried out in the following way:— First the double bottom is covered with a 3-inch layer of furnace-cinders broken into pieces of the size of a hand, and deprived of dust and small pieces by means of a coarse riddle. On the top some smaller cinders are put, so as to level the surface. Upon these the black ash is tipped in smaller and larger lumps till the tank is nearly full, and is levelled by means of large hooks till no large pieces stand out. The men's hands for this work are protected by pieces of leather from being cut by the sharp edges of the pieces. The tanks must never be filled so far that the black ash is not completely covered by the strong liquor first running upon it; any odd projecting pieces must be pulled down by hooks, lest the moist calcium sulphide be oxidized. Suppose (in the set of tanks A, B, C, D, fig. 198) D to be the tank just filled. Probably tank A will now have been worked off so far that the liquor running out of it shows only about 1° Tw. Its liquid contents are then run off by the bottom-cock into a well, and pumped up again into tank B. Some makers do not think it worth while to do so, because this weak liquor contains more sulphide than carbonate; they therefore run the weak liquor to waste and start tank B at once with pure water. According to Davis (Chem. News, xxxii. p. 187), a sample of this weak liquor, of spec. gr. 1·005, contained per litre:—

Fig. 198.



Sodium hydrate	2·640	grams.
„ carbonate	1·060	„
„ sulphide	2·690	„
„ hyposulphite	0·554	„
„ sulphate	0·284	„
„ chloride	6·780	„
„ silicate	0·100	„
„ aluminate	0·108	„
Total	14·216	„

In any case some warm water is run into B from the commencement along with the weak liquor; so that the temperature at the surface in summer is 32°, in winter 37° C.; at some works it is as high as 40° or even 43°, but certainly not higher. When working with steam, the tank B is not heated at all; nor is this done when the soda has to be as free as possible from caustic and sulphide—for instance, for sale to bleach-works. Since tank B is from the outset filled with weak liquor, this by the water run in at the top is forced into the overflow pipe, and that from the top downwards; so that the strongest portion of the liquor rises in the pipe and overflows into tank C. In this it forces the liquor, which is again heavier, through the overflow pipe over into D, which as yet only contains dry balls, but gets gradually filled with liquor; this on flowing through the fresh black ash becomes still more concentrated. Here also the liquor gets warmer, partly from the heat of the black ash itself, partly from the chemical reaction on the hydratation of sodium carbonate, and, so far as any quicklime is left, also from its hydratation and causticizing action on soda. The temperature of the liquor, measured at the outflow, may here rise to 58° or 60° C.; beyond this it is dangerous to go. When tank D has been "covered" (that is, filled to the level of the running-off pipe *f*, fig. 195 or 197), the strength of the liquor is tested. Usually it is allowed to run off at a minimum of 46° Tw. If it is not up to this strength, the outlet plug of *f* is not opened, and the tank is allowed to stand a little in order to get stronger; during this time the water must be cut off at B as well, less that tank should run over. Usually this stoppage does not last long; in sets of five or six tanks, where four or five are always actually at work, stoppage for this purpose is never necessary. When the liquor has got up to 46° Tw., it is

caused to run out of D by a supply of water running into B. The liquor at first continues to increase in strength, usually up to 52° or even 55° (measured hot). It never ought to be allowed to get beyond 57°; for this can only be attained by standing too long on the black ash; and liquors of more than 60° are always full of sodium sulphide and are coloured dark yellow or green by ferro-sodium sulphide. The lighter yellow a liquor, the better it is; quite colourless it will hardly ever be. It must accordingly be controlled by its colour, strength, and temperature; moreover some of it should be analyzed in the laboratory at least once a day.

Gradually the liquor becomes weaker again; and when it has got down to 42° Tw. (some even stop at 46°), its running is stopped. In the meantime the damp contents of A have been cast out, and this tank has been thoroughly cleaned, the false bottom removed, and the space underneath rinsed out with a jet of water. This cleanliness greatly contributes to the production of good liquors. After that the false bottom has been put in, the tank filled with black ash; and thus all is ready by the time that the strength of the liquor running out of D has gone down too much for it to be admitted into the boiling-down pans. Now the running-off plug of D is put in, its overflow plug (*e* in fig. 195 or 197) is opened, and the liquor must now flow over into A, where it acts exactly in the same way as it previously did in D. In the meantime the liquor flowing over from B to C has become too weak, viz. 1° Tw.; hence the overflow is plugged, C is made first tank, and B is treated exactly as A was treated before. In this way a continuous rotation is brought about. The more regularly and continuously the liquors can run, the purer and richer they become; consequently stoppages must be avoided as much as possible. In English works, where there is no Sunday work, Monday's liquor is almost uniformly inferior.

It is important never to lose sight of the following points, viz.:— 1st, the proper temperature of the water running in and the liquor running out; 2nd, the proper strength of the latter (the strengths of the intermediate tanks do not matter at all, as these are regulated entirely by the strong tank; hence a description of the work with more than four tanks is quite unnecessary); 3rd, the proper washing and exhaustion of the black ash. The first two points have been already touched in the preceding; but we must now say something of the residue remaining after lixiviation, the ***tank-waste***

(vat-waste). Properly washed tank-waste can be so well recognized by its external appearance that the analysis rarely gives discordant results. It is a uniform mass, neither muddy nor too coarse, of a bluish-grey to black-grey colour; only very few pieces of a larger size than that of a pea occur in it; most of the pieces are smaller. Even the larger pieces are easily crushed. But if the tank-waste shows coarser, especially hard pieces of the size of a hazel-nut and upwards, it is badly washed and there must be a considerable loss of soda.

The *chemical examination of tank-waste* usually extends only to the soluble sodium salts, and is made in this way:—A very good, large average sample is reduced to 50 grams, which are shaken with 750 grams of water at 37° or 40° C. for half an hour in a litre-flask; this is then filled up to the mark, and its contents allowed to settle. Of the clear liquor 100 cub. centims. (=5 grams tank-waste) are evaporated to dryness in a porcelain dish, a little ammonium carbonate being added to precipitate the soluble calcium salts; then the mass is heated to drive off the ammonium salts, dissolved, filtered, and titrated for alkali. More than 0·2 per cent. soluble Na_2O the waste from chalk black ash should never show; bad waste shows 0·5 to 1 per cent. and upwards. Waste from limestone black ash nearly always contains more soda than that from chalk balls; and with it the above figures will mostly be exceeded.

Now and then it is interesting and even important to test the waste for *insoluble* soda. This can be done easily and quickly in the following way:—The waste is heated with sulphuric acid of about 110° Tw., in a porcelain or even in an iron dish, till it is completely decomposed and converted into a stiff paste. This is evaporated to dryness, heated till all free sulphuric acid is expelled, hot water added, and the contents of the dish scraped out with a wooden spatula into a glass cylinder holding 250 cub. centims. Here a little milk of lime is added, made from common lime by pouring off the first alkaline waters; by this any free acid remaining is saturated, and magnesia is precipitated. The cylinder is filled up to the mark, allowed to settle; 50 cub. centims. of the clear liquid (now containing chiefly alkaline sulphates) is taken out, 10 cub. centims. of saturated baryta-water added, the liquid decanted from the precipitate through a dry filter, 50 cub. centims. of the filtrate treated with a current of carbonic acid to precipitate all the baryta; the liquid is boiled to decompose any barium bicar-

bonate, filtered, and the filtrate (now containing all the sodium as carbonate) tested alkalimetrically. If the bulk of the residue in the 250-cub.-centims. bottle is not taken into account, each cub. centim. of normal HCl would indicate 1 per cent. Na_2O in the waste, if 18·60 grams of this have been operated on; experiments made by Mr. Rennoldson, of the Tyne Alkali-Works, South Shields, have shown that only 17·71 grams need be taken, to account for the bulk of the waste.

Complete analyses of tank-waste will be given in the 14th Chapter, entirely devoted to it.

The treatment of revolver-balls in lixiviation is rather different from that of ordinary black ash, because here warm water does not suffice for exhausting the balls, notwithstanding the presence of quicklime, which loosens them, as previously described. In this case steam is always employed, and in the following way. In each tank there are, in two opposite places, steam pipes coming from above and reaching down about 18 or 24 inches, so that they dip very little below the surface of the strong liquor. (This is shown in fig. 197.) The fresh water in the weak tank is employed quite cold in summer, or at about 20° C. in winter. But by injecting steam the liquor in the strong tank is kept at 60° or even 65° C.; and by it the hard balls are so far disintegrated that they become easily accessible to further lixiviation. The temperature in the tank just preceding the strong one is by occasional injection of steam, especially just before turning its contents into the strong tank, kept at 37° or 40° C. In all cases the lixiviation of revolver-balls requires much more attention than that of ordinary black ash.

Other proposed lixiviating-apparatus can be treated very shortly, as none of them can compete with the cheap and simple Buff-Dunlop apparatus, which does every thing that complicated apparatus can do. That of Havrez (Bull. Soc. d'Encour. 1867, p. 485) consists of cylindrical tanks, 1½ to 3 feet high and 3 to 10 feet in diameter, with an axis consisting of a pipe from which radial partitions start, dividing the tank into twelve sectors, two of which always work together. A peculiar cock in the central tube permits the circulation of the water and the liquors to be systematically changed. Its principle is not different from that of the Buff-Dunlop apparatus; and it does not seem at all well adapted for work on a large scale.

Another apparatus, proposed by Schwind (Dingler's Journ. cxcviii.

p. 127), is to facilitate the continuous supply of the material to be lixiviated. This is hardly feasible, for black ash at any rate.

An apparatus by H. Fischer (Dingl. Journ. ccxviii. p. 485) consists of a large ring bearing four tanks suspended within it at equal distances, the ring being turned round by machinery. This apparatus does not seem at all adapted for black ash.

The tank-liquor as it flows away from the strong tank is too muddy to be boiled down directly. It must be completely settled in special settlers, in which all the tank-waste mechanically carried away will be deposited along with a little iron sulphide arising from the decomposition of ferro-sodium sulphide and an insoluble aluminio-sodium silicate.

Davis (*l. c.*) gives the following analysis of such a sediment carefully washed and dried in a current of hydrogen (*a*), together with the analysis of a crust that formed in the settlers and, in greater quantity, in the boiling-down pans (*b*) :—

	(*a*)	(*b*)
Silica	23·60	39·572
Alumina	18·34	33·584
Sodium oxide	13·22	20·776
Water	...	5·844
Iron sulphide	5·84	...
Calcium sulphide	38·00	...
	99·00	99·776

By the action of *carbonic acid* (for instance when the settlers are heated by waste fire-gases passing over them), Scheurer-Kestner observed, a white pulverulent aluminium silicate (32·2 SiO_2, 43·45 Al_2O_3, 23·93 H_2O) was formed.

Care must be taken lest the liquors in the settlers should cool down to any extent, because in that case a large portion of the soda would crystallize out in an impure state. For this purpose, *e. g.*, the settlers may be placed over the ball-bank, where the heat of the balls will act upon them, or over the boiling-down pans; or they may be arched over, and the fire-gases coming away from the boiling-down pans behind the ball-furnaces may be passed over the surface of the liquid, in which case the fine drops of liquor thrown up in boiling and carried away by the draught will be recovered. In any case the settlers must be large enough to

admit the complete deposition of the mud. The better the liquor is settled, the stronger and whiter the soda will be, and especially by the decomposition of the ferro-sodium sulphide. Either several settlers are provided which are alternately filled and emptied, or the settlers are made very long, and the liquor is run in at one end and gradually run out at the other. They are always mounted so high that they can immediately feed the boiling-down pans; consequently the liquor has generally to be pumped into the settlers. Hence the tank-liquor usually flows from the tanks into a well, generally made of cast iron—which need not be at all large, as the pump is constantly working. This pump (which of course must be made entirely of iron, without any brass parts) is placed just above the well, so that any liquor leaking out or overflowing runs back into the well. The pump-barrel and the delivery-pipe must be emptied every time after being used, lest they should be stopped up by crystals.

Composition of Tank-liquor.

It is very advisable to make a daily analysis of the tank-liquors, which need not embrace all its constituents (a matter obviously impossible), but only so far as to get an idea of its essential composition and of that of the alkali to be obtained from it. This has been done very quickly and with quite sufficient accuracy in the author's laboratory for many years past in the following manner:—The tank-liquor is employed in the warm state, just as it comes from the works; or, if necessary, it is heated again till all crystals have dissolved. Samples of only 1 cub. centim. each are taken by means of a pipette divided into hundredths; by taking such small quantities, great speed of execution is secured, with sufficient accuracy. First 1 cub. centim., diluted to 10 cub. centims., is boiled with an excess of standard sulphuric acid till all CO_2 and H_2S are expelled, then litmus solution added, and standard soda solution run in till the mixture is just neutralized. If litmus is added at first, it is discoloured and rendered useless by the H_2S; but by the azo-dyes (Vol. I. p. 48) this drawback is avoided, and the liquor can be titrated directly, without going back, with standard soda solution. Thus the total alkalinity is ascertained, inclusive of caustic and sulphide. Another cubic centim. is diluted, some standard solution added, and decinormal iodine solution run in up to blue: this shows Na_2S; the minimal quantities of sulphites and hyposulphites

occurring in fresh tank-liquor are also measured with it, and can without sensible error be calculated as Na_2S. The number of cub. centims. of iodine solution found is divided by 10 and deducted from the number found for normal acid. This gives the amount of caustic and carbonate which were present; these are both calculated as carbonate, because they occur as such in the alkali. In a third sample the sodium chloride is estimated as follows:—1 cub. centim. is taken out, exactly as much normal sulphuric acid run in as was required in the first experiment to neutralize the liquor; the liquid is boiled till *all* H_2S is driven off, passed through a small filter to remove the sulphur precipitated, once washed; to the neutral liquid some yellow potassium chromate solution is added; and it is titrated with silver nitrate till the red colour appears. Lastly, the sulphate is estimated (best in 2 cub. centims.), either according to Wildenstein's plan or gravimetrically, which with this very small quantity (at most 0·060 gram $BaSO_4$) takes only 20 minutes, if the liquid is precipitated boiling hot, filtered at once by help of the long funnel, fig. 199 (which greatly hastens the operation), washed with boiling water, the small filter with the precipitate placed for a few minutes on a hot place, till it can be taken out and put into the platinum crucible, lying on its side; the flame of the burner is gradually moved from the mouth of the crucible to where the filter is lying, till the latter is burnt and all is red hot. The operation is finished by cooling the crucible on a stone and weighing; and during the boiling, washing, drying, and igniting, the above-described three tests for alkalinity, sulphide, and chloride can be carried out as well. This of course supposes that boiling water is at disposal, and that the platinum crucible is tared (which is best done by means of a piece of copper or lead, corrected from time to time so as to make it agree with the decreasing weight of the crucible).

Fig. 199.

The way of calculating the results will be most easily understood from a particular instance. Suppose it has been found that

(1) 1 c. c. requires 6·1 c. c. normal sulphuric acid,
(2) 1 „ „ 1·5 „ decinormal iodine solution,
(3) 1 „ „ 1·8 „ decinormal silver solution,
(4) 2 „ yield 0·045 gram $BaSO_4$.

First, from 6·1 is deducted $\frac{1·5}{10}$=0·15, leaving 5·95 normal acid for sodium carbonate (+hydrate).

From this follows:—

1.	5·95	×	0·513	=	0·3053 gram	Na_2CO_3
2.	1·5	×	0·0071	=	0·0106 „	Na_2SO_4
3.	1·8	×	0·00585	=	0·0105 „	NaCl
4.	0·0225	×	0·609	=	0·0137 „	Na_2SO_4
					0·3401	

The item 2 is at once calculated as sulphate, because in the further operation the lower oxides of sulphur are mostly converted into it. Item 4 (Ba_2SO_4) is divided by 2, as it is obtained from 2 cub. centims. liquor, and multiplied by 0·609 in order to get from $BaSO_4$ to Na_2SO_4.

The numbers found now show what fractions of a gram of carbonate, chloride, and sulphate the alkali, to be obtained from that liquor, will contain; and if all the figures are added up, the total solids is obtained, viz. 0·3401 in our particular instance; and by the ordinary rule of three are calculated the percentages of this alkali, viz.

89·8	Na_2CO_3
3·1	NaCl
3·1	Na_2SO_4 formed from Na_2S
4·0	Na_2SO_4 contained as such in the liquor.
100·0	

This calculation cannot be regarded as quite exact, even for this reason—because ordinary soda ash contains from 1 to 1·5 per cent. of insoluble constituents; but as, on the other hand, by well carbonating the liquors at least a portion of the Na_2S is not, as here assumed, transformed into Na_2SO_4 but into Na_2CO_3, the above

error is so far compensated that an almost absolutely reliable indication of the strength of the alkali to be expected is obtained.

If the caustic soda in the tank-liquor is to be estimated separately, 2 cub. centims. of the same are diluted with hot water in a 100-cub.-centim. flask, barium chloride added to excess, the flask filled up to the mark, allowed to stand for a moment till the precipitate subsides (which it does very quickly in the hot liquid), the clear portion poured through a dry filter into a 50-cub.-centim. flask, and the filtrate titrated with standard hydrochloric or nitric acid, which only indicate the NaOH originally present.

From the above tests the following conclusions can be drawn:—Above every thing, of course the alkalimetrical titre of the liquid should be a high one. If too much common salt is found, this is of course not the fault of the black-ash process, but of the decomposing department; and the quality of the sulphate accordingly should be improved. If too much iodine solution has been used, it will either be the fault of the black ash, many "red" balls having been present, or else the lixiviating-tanks have gone too hot or stood too long. A high figure for barium sulphate is nearly always caused by bad, burnt, or "soft" balls, and is mostly accompanied by a high figure for iodine. High causticity points to too much coal in the balls and too hot lixiviation.

Recently, since so much attention has been drawn to the *cyanides* in black ash, testing the liquor for them has become a matter of importance. This matter has been treated by Hurter (Chem. News, xxxix. p. 25), whose description will be given *in extenso*.

In soda lyes there may occur sodium ferrocyanide, sulphocyanide, and cyanate; the cyanide originally present as such in black ash must have been transformed into ferrocyanide during the lixiviation. If, however, any sodium cyanide is present at all, it is readily converted into ferrocyanide by boiling the liquid with freshly precipitated ferrous oxide (produced by adding a little ferrous sulphate to the alkaline liquid). The cyanate and sulphocyanide are not of any importance, as they yield colourless products of decomposition during the further treatment of the soda; the ferrocyanide alone requires to be estimated. This can be done very rapidly by the following method, sufficiently accurate for solutions containing not more than 2 grams of sodium cyanide per litre.

When soluble ferricyanides are mixed with copper salts, yellow

copper ferricyanide is formed. If a proto-salt of iron is added afterwards, a blue precipitate will be formed so long as any ferricyanide exists in solution; but beyond that point the ferrous salt reacts upon the copper ferricyanide, reducing it to ferrocyanide, thus:—

$$Cu_3Fe_2Cy_{12} + 2HCl + 2FeCl_2 = Cu_3H_2Fe_2Cy_{12} + Fe_2Cl_6.$$

This reaction is made use of as an indicator. 100 cubic centimetres of strong soda-liquor is treated with a bleaching-powder solution till all sulphides &c. are oxidized into sulphates, and ferrocyanide into ferricyanide; the solution, after being acidified and freed as much as possible from excess of chlorine by warming and agitating, is ready for titrating.

On a porcelain slab sprinkle a few drops of a dilute solution of ferrous sulphate (1 : 100). Add now to the solution to be analyzed a decinormal copper solution from a burette until a drop of the liquid, brought into contact with a drop of ferrous sulphate solution, no longer gives a blue colour, but the pure purple colour of cupric ferrocyanide. The copper solution is prepared by dissolving 3·17 grams of copper in as little nitric acid as possible, and diluting to 1 litre; each cub. centim. of it $=0{\cdot}01013$ gram Na_4FeCy_6.

If the copper ferricyanide is present in larger quantities than those indicated above, it hides too much the colour of the Prussian blue. Moreover in concentrated solutions the composition of the precipitate is not exactly $=Cu_3Fe_2Cy_{12}$.

Sulphocyanide rarely needs estimating, as it is comparatively harmless and only present in traces. It can be approximately estimated by acidifying the tank-liquor, precipitating the ferrocyanide by zinc chloride, filtering, colouring the filtrate by ferric chloride, and comparing the colour with that produced in ferric chloride solution by a solution of potassium sulphocyanide of known strength.

One of the most disagreeable constituents of tank-liquors is the *iron* which occurs in them in various forms, and imparts to the soda ash made from them a yellow or a reddish colour. If the iron could be entirely removed from the tank-liquor, crystal soda and white alkali could be made directly from the liquors, whilst till very recently these could only be made by the expensive process of boiling down, calcining to soda ash, and redissolving the latter. By means of very good black ash, long settling, and thorough car-

bonating, a few works had already arrived at making crystals direct from tank-liquors; but such crystals are said to have been always soft and with difficulty saleable. Whether the new Pechiney-Weldon-process will do away with this drawback, a little more experience alone can show.

Analysis of Tank-liquors and Salt-residues from the same.

	From Stolberg. *Mohr.* Per cent.	From Duisburg. *Mohr.* Salt-residue. Per cent.	From an English works. *Brown.* Salt-residue. Per cent.		English works. *Davis.* Grams per litre of liquor.	
Sodium carbonate	23·60*	71·250	68·91	65·51	209·500	204·326
„ hydrate	...	24·500	14·43	16·07	44·800	52·740
„ chloride	0·50	1·850	3·97	3·86	19·597	23·412
„ sulphide	0·13	0·235	1·31	1·54	4·485	3·822
„ sulphite	...	0·102	2·23	2·13	1·323	0·979
„ hyposulphite	0·30	0·369	trace	trace	1·580	1·774
„ sulphate	0·23	... †	7·02	7·81	12·707	14·258
„ cyanide	...	0·087	...	...	...	...
„ ferrocyanide	...	...	...	...	0·133	0·416
„ sulphocyanide	...	...	...	...	0·211	0·196
„ aluminate	...	...	1·03	0·80	3·371	4·218
Alumina	...	1·510	...	...	...	...
Sodium silicate	...	...	1·02	1·23	5·961	3·774
Silica	...	0·168	...	...	...	...
Sodium phosphate	...	...	...	...	traces	traces
„ fluoride	...	...	...	...	traces	traces
Iron sulphide (dissolved)	...	traces	...	...	0·074	0·042
Insoluble in acids	...	...	0·81	0·97	...	...
Total	24·76	100·071	100·73	99·92	303·742	309·957

* Inclusive of NaOH.

† There must be an error here; liquors entirely free from sulphate are not known. The analysis as published in 'Dingler's Journal,' cliv. p. 205:—Total solids 24·98 per cent.; specific gravity of the liquor 1·25.

The iron is in the first place found as *ferro-sodium sulphide,* a compound frequently investigated, especially by Berthier (Ann.

Chim. Phys. xxxi. p. 170), Stromeyer (Ann. Chem. Pharm. cvii. p. 333), Maumené (Compt. Rend. lxi. p. 846), E. Kopp (Bull. Soc. chim. v. p. 207), Schneider (Pogg. Ann. cxxxviii. p. 302). The influence of this compound in tank-liquor is the main subject of a paper by Kolb (Ann. Chim. Phys. x. p. 106). According to him, metallic iron is not acted upon by sodium hydrate, carbonate, or even sulphide [?]; neither is ferric oxide or iron monosulphide by sodium hydrate or carbonate [?]; but the two latter with sodium sulphide yield ferro-sodium sulphide; ferric oxide, along with this, also caustic soda. The sulpho-salt by itself is black, but remains long suspended in solutions of sodium hydrate or carbonate, and colours them green or brown according to the degree of concentration, for which even a few millionths are sufficient. A solution of 0·016 gram FeS with 0·090 gram Na_2S in 100 cub. centims. water is blackish green, in 4 litres of water bottle-green, in 8 litres pale green; and even in 16 litres it is perceptibly coloured. Its solubility (apparent or real) is much greater in concentrated than in dilute liquors; on diluting, the former a portion of it at once separates as a black precipitate. It is also more soluble with heat; yellowish-brown clear hot liquors on cooling become muddy and slowly deposit a black precipitate. Also sodium chloride or ammonium salts precipitate the sulpho-salt with decolorization of the liquid: therefore liquors rich in common salt are little coloured. Although itself black, the sulpho-salt imparts a yellow or red colour to white salts, if finely divided among them; 1 gram of it suffices for colouring 100 grams of perfectly white alkali yellow, 5 grams for colouring it brick- or purplish red. Sometimes a liquor coloured by it, on being boiled down and the residue calcined, yields a white ash, which, however, on lying in damp air becomes coloured again. Soda ash containing iron also frequently comes out white from the calcining-furnace, but on cooling down assumes a yellow colour. [This is especially noticed on the surface of the heaps.] Exposed by itself to damp air for some time, the salt gradually becomes of a dirty green, and at last of an ochre-colour; and in it hyposulphite and ferric hydroxide are formed. For the practice of alkali-making the following lesson can be drawn from this [which was acted upon by many practical men long before Kolb], viz. that the liquor is not to be boiled down at once, but as much as possible of the sulpho-salt removed from it. Kolb's way of doing this, cooling down in a dilute state, is not suitable for

practice; neither is the addition of ferrous sulphate, which decomposes the sulpho-salt into sodium sulphate and insoluble FeS—any excess of ferrous sulphate being very injurious. Spathic iron-ore (native iron carbonate), recommended by Habich (Dingl. Journ. cxl. p. 370), is far too little energetic, and has entirely failed. Other metallic oxides and salts have been proposed (all of which, in removing all sulphide, also destroy the ferro-sodium sulphide and precipitate the iron), *e. g.* zinc oxide and carbonate by Parnell (patented Sept. 2nd, 1870), lead oxide by several, ferric hydroxide by Deacon: he employs it in a liquor of about 70° Tw. at a temperature of only 20° C., since he finds that the liquors are coloured if heated in the presence of the metallic sulphide; the iron hydroxide &c. are to be brought into intimate contact by violent churning. Ammonium carbonate, proposed by Margueritte for decomposing the sodium sulphide and sodium bicarbonate, removes both the latter and the caustic soda, but is too dear. At Dieuze lead sulphate is employed, by which the ferro-sodium sulphide is decomposed, leaving lead sulphide and sodium sulphate. In practice, at any rate in the manufacture of soda ash, *oxidation by air* is employed almost exclusively as the desulphurizing means, best along with carbonic acid to decompose the Na_2S, and still better in conjunction with MnO_2 (Pauli's process). We shall treat of this later on. Besides, as a *preventative* against the formation of Na_2S, the addition of limestone dust at the end of the balling process is recommended in Weldon's patent, p. 421.

A shape in which the iron adheres even more tenaciously to the liquors, oxidation by air &c. being unavailing, is that of *sodium ferrocyanide,* the formation of which by the nitrogen contained in the coal, especially at a moderate temperature, has been mentioned on p. 371. On calcination this salt is destroyed; and the resulting ferric oxide colours the ash more or less. In order to remove the ferrocyanide, Gossage has proposed a peculiar system of evaporation (see below), which, however, has not been successful. Williamson (patent of Dec. 6, 1866) removes it by heating the strong liquor in an iron steam-boiler to 155° C., at which temperature the salt is destroyed and the iron separated in an insoluble shape. As soon as the pressure within the boiler has got up to 5½ atmospheres, samples are to be drawn from time to time and tested for ferrocyanide. This process failed on account of being too expensive; the worst drawback was, that during the operation a hard crust was

formed at the bottom of the steam-boiler, which could not be removed by any means, and quickly destroyed the boiler. Could not this be remedied?

It is, however, possible from the outset to almost entirely exclude the formation of ferrocyanide by employing Pechiney's improvement of the balling-process (described on p. 421), as is shown by the analyses on p. 452.

CHAPTER VIII.

BOILING DOWN THE TANK-LIQUOR, AND CALCINING.

The tank-liquor is always concentrated by boiling it down—either evaporating it to dryness just as it is, and then converting it by calcination into a commercial product, or so that its solid constituents are divided into several portions of unequal quality. In the former case pans heated from the top, in the latter case pans heated from beneath are usually employed; there are, however, exceptions to this rule.

The construction of the *pans heated from the top* (*open pans*) need not be entered upon here, since it has been described and represented by diagrams in connexion with various black-ash furnaces, by the waste heat of which such pans are always heated (pp. 389 and 412). We need therefore only describe the work in these pans. Before using them, first the doors have to be put on. As they cannot well be made to join tightly metal upon metal, and the ordinary means of making joints tight cannot resist the hot and very caustic liquor, a putty made of pure lime or of clay is employed for this purpose. Lime does not stand as well as clay; but with the latter the greatest care has to be taken lest on drawing up the screw, when the superfluous clay is squeezed out, or later on, when taking away the door, any clay should get into the drainer and be calcined along with the salt; for in that case the ash will be contaminated by the red burnt clay.

After putting on the doors the pan is filled with clear settled liquor from the settler, which is always fixed at a higher level; and its contents are now left to the action of the fire-gases coming from the ball-furnace. These soon raise the temperature of the liquor to the boiling-point—and cause a rapid evaporation, because the

vapours formed are at once carried away by the draught and do not interfere with the action of the flame on the surface of the liquid. The draught certainly causes the loss of minute drops of liquor thrown up in boiling, whose salts collect as crusts and deposits in the flues. These can be saved if the settlers are arranged as described on p. 48—that is, if the flame leaving the pans travels over the top of the liquor into the settlers, or if this flame is used for carbonating the liquor (see below). On the other hand, the draught easily carries away some particles of the black-ash mixture, especially of sulphate, and also light ashes from the fire, into the pan, which contaminate its contents.

The fire-gases act both in a useful and in an injurious manner—the latter especially by their sulphurous acid, so far as this has not been absorbed in the ball-furnace itself. We shall later on see, from Moorhouse's researches, that this contamination is not so bad as is usually assumed—viz. that it only brings 0·1 or 0·2 per cent. of sulphur into the soda ash, including the sulphate mechanically carried over. According to experiments made by Hasenclever (Chem. Industrie, 1878, p. 8), the fire-gases in a six-hours' trial contained on entering the pan 0·0043 gram SO_2 per litre, and only 0·0032 gram on leaving. On the other hand, the carbonic acid, occurring in a much larger proportion, acts usefully by carbonating a portion of the caustic and the sulphide; but this action is nothing like so strong as is usually assumed; this will easily be understood, as the escaping vapour much diminishes the direct contact between the fire-gases and the liquor. Partly for this reason, it is not very usual to make caustic from the "red liquors" obtained in open pans; but the author himself has done this on a large scale; nor does there appear, when the analyses of such liquors given below are examined, any reason why it should not be done. At Aussig caustic is regularly made from red liquors obtained in open pans.

The pan is filled with liquor nearly up to the angle-iron surrounding its upper edge, and filled up several times, according to whether it is to be drawn once every 24 or every 48 hours. The former is to be preferred, and, with fair draught, is easy of attainment. The liquor of course boils most strongly at the side next to the furnace; and on this side most of the salt is separated as soon as the liquor has been sufficiently concentrated. The work of the panmen consists in moving from time to time, towards the back of the pan, the salt forming in its front part, by means of iron rakes

(with a head 12×6 inches and a shank 12 feet long and 1 inch thick) introduced through the upper, free openings of the doors, and in pushing down into the liquor the crusts of salt forming on the surface, as otherwise all evaporation would cease. The pan is finished when the separated salt reaches up to the surface and its contents have been converted into a mixture of the consistency of mortar. Now the screw-bolts fastening the doors are slackened, and the men wait a few minutes till the liquor still standing among the salt in the pan has run out into the drainer through the chinks thus formed; then the doors are taken off altogether, and the "black salt" is drawn as quickly as possible into the drainer, one man working at each door. The doors are put on again immediately, so as not to interfere with the draught in the ball-furnace, and the pan filled up again. When there are two parallel pans, that which is being drawn is cut off from the draught altogether, so that the furnace is not interfered with at all.

The quantity of black salt drawn from a hand-furnace corresponds to 25 or 30 cwt. of soda ash; in any case each furnace must boil down as much liquor as is obtained from the black ash made in it.

The open pans last many years without repairs if they are well and substantially made from the first and their ends protected in setting. The bottom suffers least; but on the sides hard crusts of salt soon form, which must be removed at once, in order to avoid burning the pan by overheating it. This is much facilitated by building into the pan-arch, near the edge, a few cast-iron boxes, ordinarily closed by a cover, through which a long chisel for breaking off the crusts can be introduced.

An improved method of collecting the salts has been patented by J. C. Stevenson (No. 4148, Oct. 18th, 1878). A number of vessels or pockets are placed below the level of the pan, communicating with the same by apertures, which may be closed by plug valves. Only one or some of the pockets are open at a time, and of course filled with liquor from the pan. As the evaporation goes on, the salts are raked to the plug-hole and fall into the pocket, gradually displacing the liquor. When one pocket is full of salts, its plug is put down and another pocket is opened to receive in its turn the salts from the pans. The liquor in the pockets is drawn off by a tap in the bottom; and the salts, when sufficiently drained, are removed by opening a water-tight door. The draining-tap is then shut and

the door closed; and the plug being lifted, the pocket fills with liquor from the pan, ready again to receive the salts. A pipe in the top of the pocket allows the escape of air when the pocket is being filled with liquor. In the meantime the other pockets are shut off and their contents allowed to drain.

The "black salt" consists essentially of monohydrated sodium carbonate, mixed with a little chloride and sulphate and soaked with mother liquor, which is called *red liquor* (from its colour, due to iron sulphide and organic substances). The latter contains most of the impurities, and is actually richer in caustic than in carbonate. A sample obtained by the author from a pan heated by top heat, of specific gravity 1·334, contained :—

			grams per litre.	per cent. by weight.
Soda (Na_2O)	as	$NaOH$	167·4	12·6
"	"	Na_2CO_3	40·3	3·0
"	"	Na_2S	15·5	1·2
"	"	$Na_2S_2O_3$	6·2	0·5
"	"	Na_2SO_4	3·0	0·2

(The chloride had not been estimated; many other analyses likewise showed a proportion of 4 to 1 between the soda occurring as hydroxide and carbonate.)

The more red liquor drains off the salt, the better it is; and as there is not time for thorough draining in the pan-drainers between two drawings of the pan, there should be separate black-salt drainers, into which the salt should be moved from the pan-drainers and remain there two or three days before calcining. Only by good draining can strong ash be made. When the carbonating is done by sawdust, the latter is already put in the pan, and facilitates the draining of the salt. This is regularly done on the Tyne, but only exceptionally in Lancashire.

Well-crystallized, coarse-grained salt drains much better than fine-grained or muddy salt, and yields better ash. Its colour should be greyish white, not dark grey or reddish yellow; the former is due to bad settling, the latter to ferro-sodium sulphide.

If especially strong ash is required, the black salt is sprinkled over with water to displace the red liquor. Centrifuging the salt, as proposed by Gamble, acts even more thoroughly, but is rarely applied (*e. g.* in a few works near Liverpool and at Rouen),

as the manipulation of such a caustic salt is unpleasant. Ralston (patent of Nov. 15th, 1860) proposed to systematically wash the black salt by means of a concentrated pure solution of sodium carbonate. This first removes the caustic and ferrocyanide with a little chloride and sulphate, on prolonged washing also the chloride, and at last the sulphate. Ralston for this purpose proposed a series of iron tanks in which perforated boxes for receiving the black salt were to be suspended, and a solution of pure sodium carbonate circulated through them in the same way as black ash is lixiviated. This plan does not seem to be followed in practice; but another plan, also proposed by Ralston, is actually carried out in some places, viz. treating the black salt with steam in a closed vessel, and draining off the condensed solution. The salt thus gains several degrees; and this plan is applicable to "fished salts" from boat pans as well.

Although, as we have seen, there is no reason why red liquor from open pans should not be worked up for caustic, this, at least in England, is not very usual; it is regularly pumped back into the pans and concentrated along with the next batch. It is often suitable not to charge each pan with its own liquor, but to keep it out of some of the pans and to concentrate all the red liquor in the other pans. Thus, for instance, instead of an average make of 52 degrees, which in England is considered very fair for hand-furnaces, two qualities will be obtained—one of 53 or 54 degrees, and another of from 48 to 50 degrees. Such a separation is regularly made in revolver-pans, and the stronger salt got up to 56 or even 57 degrees.

Since a little fine salt always passes through the holes in the double bottom of the drainers (which are made about $\frac{1}{16}$ inch wide), and collects below that bottom as a kind of mud, the latter must not be allowed to accumulate till the whole space below the false bottom is filled up; for then the red liquors cannot drain off and will remain in the lower strata of the black salt. Hence from time to time the very disagreeable labour of lifting the drainer-plates and clearing out the caustic mud has to be performed. It is often calcined by itself to a low-quality ash; sometimes it is charged into the lixiviating-tanks, which it disarranges a good deal; the best plan of all is to pass it through the black-ash furnaces, a little of it with each ball.

In Lancashire open pans are sometimes worked by *fishing*. In

this case the pans have not open pockets projecting in a rectangular way as shown in the previous diagrams, but pockets with a slanting-up bottom, as shown in fig. 200 from the top, and fig. 201 in section. There are no doors required here, as the liquor cannot run out in any case. The salt accumulating is constantly drawn towards the pockets, the open top of which projects from

Fig. 200.

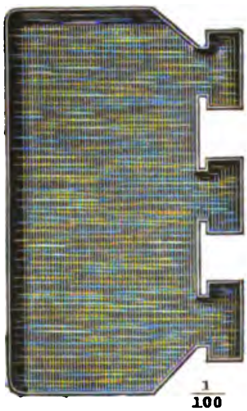


Fig. 201.

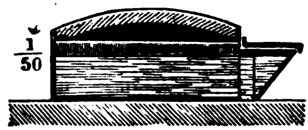


Fig. 202.

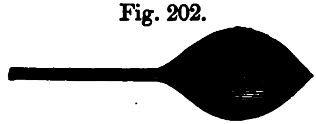


Fig. 203.

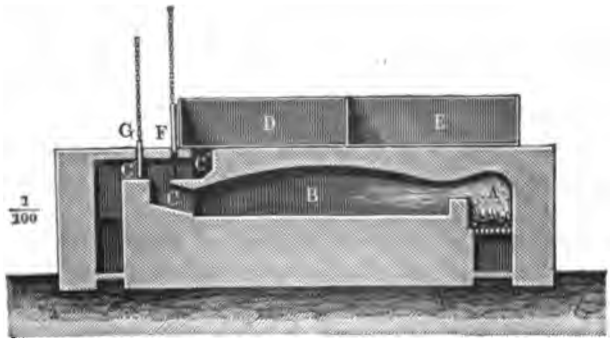
the pan-arch, and gives free access for working in it. Then a workman dips a large "fishing-shovel" (figs. 202 & 203), with a concave blade pierced with many holes, into the pocket, scoops out the salt, lets it drain a little, and by a quick movement throws it behind him onto a stage fixed at some elevation, whence the drainings run back into the pan. In this operation some salt and liquor are easily spilt; and it does not give the impression of cleanliness. Of course the pan drainers sunk in the ground, as previously described, might be employed here also; and this in fact is regularly done when "fishing-pans" are employed in boiling down the liquor for refined alkali, where the luting of the doors with clay or lime-putty is sought to be avoided by the employment of the pockets as in figs. 200 & 201.

Another kind of evaporation by open fire is frequently carried out in France in the "Marseilles furnaces," for obtaining *caustic ash* (*sels caustiques*)*, as shown in fig. 204. Each furnace has two

* This article is used in France for washing body-linen; but it must for this purpose be quite white and free from iron. A higher price is paid for it than for

pans, D and E, communicating with each other and heated by the fire of the furnace A B C. They are filled with settled liquor, which is brought in them up to 60° or 62° Tw. (measured hot) and then

Fig. 204.



run into the furnace itself. Its bed either consists of firebricks or of cast-iron plates. In the former case it is covered with a thick layer of dried soda-salt; in the latter it is made of small square plates of cast iron closely put together, because a single plate could not be kept from cracking.

The flame passes through the snore-hole C, either into the flue C′ and thence into the chimney, or into the flue C″, heating the pans D and E; the dampers G and F permit doing either the one or the other. Before running-in the liquor, care must be taken to make the furnace very hot; the fire is therefore passed directly into C. If now the liquor flows in, it is evaporated very quickly, and the furnace-bed is soon covered with a semifluid paste. From this moment the furnaceman touches the fire as little as possible; in order to prevent any coal-ashes being carried away, to lessen the heat, and to obtain a clear, oxidizing flame, he shuts the damper G, and opens F, so that the flame circulates below the pans. The pasty mass on the bed is soon covered with a reddish crust, which the man breaks up and rakes through with a tooth-rake; he thus renews the surface and facilitates the oxidation of the organic substances and the sodium sulphide. When the mass begins to harden, the tooth-rake is replaced by a common rake, and the mass heaped

carbonated ash. An inferior quality of it is used for making eau de Javelle by passing chlorine into it.

up in a place removed from the fire. The temperature now should not exceed the melting-point of lead; and care must be taken that the salt be not fused. The man crushes and granulates it as well as possible; during this it becomes quite white; and when finished it is drawn out into iron waggons. After cooling, it is passed through a coarse sieve; that which remains on the sieve is broken up by hand or crushed in cast-iron mills. Although the soda salt obtained by this process is very caustic (with a total titre of 82° Decroizilles =88·7 per cent. Na_2CO_3, it often has 16° of causticity, corresponding to more than 17 per cent. Na_2CO_3), it does not, with good work and good liquors, turn yellow or black, even in damp air.

The following particular details, derived from practice, will be welcome to some readers. The French makers, when intending to make caustic ash, mix 540 kilog. sulphate with sufficient chalk and coal, and pull this out in two balls (p. 400). They lixiviate at 40° C., only heating the tank on the surface; the liquor is left to settle for two or three days, and run into the pans perfectly clear. It ought to be of a bright straw-colour, and not turn either green or brown on cooling. On the addition of common salt no FeS ought to be precipitated; but should there be any, the liquor can be cleared from it by adding a little sulphate—which, though it lessens the strength of the ash, precipitates the FeS and makes the salt less fusible. The liquor should contain at most 1 or 1·3 part Na_2S upon 100 dry salt. It should never come to the boiling-point in the pans, or stop in them any length of time, because thus it would again dissolve some iron. The following is the composition of a liquor yielding fine white salt of 86° Decr., of which 17° are caustic:—

	grams per litre.	per cent. of solids.
Na_2CO_3	155·75	68·20
$NaOH$	41·10	18·00
Na_2SO_4	15·71	6·88
Na_2S	4·45	1·45
$Na_2S_2O_3$	0·07	0·03
$NaCl$	7·20	3·16
Al_2O_3, Fe_2O_3, SiO_2, &c.	4·12	1·80

It is best only to run enough liquor into the furnace to make four batches of 300 kilog. caustic ash per 24 hours; with very good

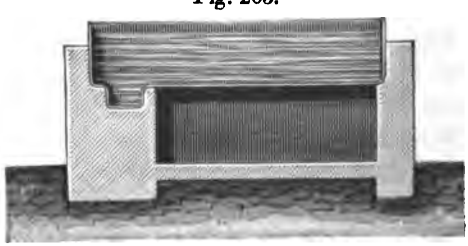
men as much as 500 kilog. can be turned out in a batch; but some works make only three batches daily. Each furnace is served by two men. When the furnace and fireplace have been charged, the damper leading towards the chimney is raised fully; the coals are sprinkled a little with water. After an hour and a half another fire is put on, and the dampers arranged so that the fire is entirely drawn underneath the pans. Now the salt already collected on the edges and the bottom of the furnace is detached, pushed behind, and the furnace-door closed. After this the flame is again allowed to pass through the furnace. In 20 minutes the liquor begins to solidify on the surface; the crusts are pushed down with a rake, the furnace closed, and this treatment repeated after 10 minutes, after which the water is almost all evaporated. The furnace is then closed again; and as the fire does not give out much smoke now, the draught is cut down a little; and as this is done after each treatment, ultimately the damper leaves to the flue only 4 inches opening. Two more operations with the rake follow; and only 2^h 10^m or 2^h 20^m after charging the furnace with fresh liquor the man begins detaching the salt from the bottom and the sides with his paddle (slice) and crushing the lumps with his rake. The fire-door is closed and the fire allowed to act for a quarter of an hour before working up the salt. At first a heavy rake, of a semicircular shape, is employed for crushing the damp and close mass. It is gradually brought forward near the fire-bridge and broken up a little; the furnace-door is closed again, and the back end of the bed left empty. Now (about 2^h 45^m after beginning the work) the desulphurization begins. The tool used here is similar to the first, but with a longer and lighter semicircular head. By means of this the salt is spread on the bed and turned over, moved from front to back, and the surface constantly changed. If more heat is needed for the less-finished portions, the furnace-door is closed for 2 or 3 minutes; but after putting on the second batch of coals (see above), the fire must not be touched again. In order that it may burn on well, very bituminous coal should be employed: that which has been found the best is the "patent fuel," made from small coal by means of coal-tar pitch; it gives out a lasting heat, and requires no stoking. About 80 parts of good coals are required for 100 caustic ash. After 3 hours' working, the desulphurization is finished; the workman tries this by means of an alkaline solution of lead, which must not blacken the

salt. The operation is the more difficult the more undecomposed NaCl and the more caustic are present; the mass is then more fusible and the fused portions surround the others, protecting them against the action of the fire-gas. The whole operation takes 5¾ hours. The salt is now drawn out, cooled, and sifted (compare what has been said above). The bed is once a week cleared of the crusts (fluxings).

Pans heated from underneath are much more frequent than those heated from the top in France and Germany, and are also found in many English works, especially those making caustic soda. Revolving furnaces are never provided with them. Evaporation by bottom heat has these disadvantages in comparison with that by top heat—that the pans suffer more, that it takes more labour, and that the heat is less completely utilized; but it has the advantage of keeping the liquor purer and of admitting a systematic separation of the products, although the latter is quite possible with open pans too. It is generally assumed that only by bottom evaporation can the best white soda ash be obtained; but in fact several works, both English and continental, by dint of great care turn out quite as white soda-ash from open pans, and even from revolvers, as others from bottom-heated pans.

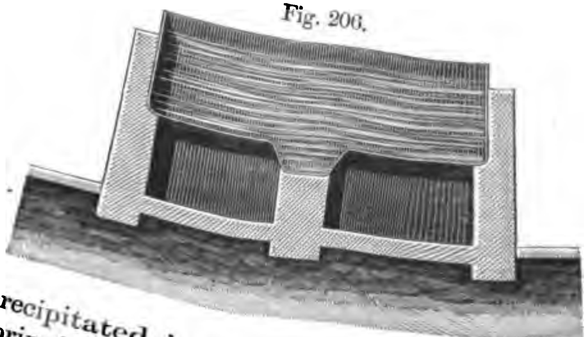
In Germany the pans heated at the bottom are flat-bottomed, of the shape of salt-pans, 20 to 30 feet long, 8 to 10 feet wide, and 18 to 30 inches deep. Sometimes at the back end of the pan a gutter is made in the bottom, to facilitate the removal of the salt (fig. 205); sometimes a central depression is made (fig. 206): the latter is a transition to the system of boat pans, but not equal to them in convenience. In most works the pans have plain bottoms and are fired like salt-pans, either by separate fires or by the waste heat of ball-furnaces. Sometimes they have a vapour-hood, which

Fig. 205.



somewhat interferes with the work, and hence is frequently l out. It is better to fix one about 2 feet above the pan, only occ pying ¼ to ⅙ of the area of the pan; if provided with a tall wood chimney, it almost completely draws away the steam without inte fering at all with the work in the pan.

Fig. 206.



The salt precipitated in boiling down here naturally settles the bottom, principally round the edges, which are not directl touched by the fire, and where the liquor does not boil so strongl The salt would soon burn fast and the pan-bottom would be quickl destroyed by the fire, unless the salt were constantly pushed off b means of sharp tools and moved to a less hot place. The latera gutter shown in fig. 205 is very irrational, because it gives the sal all the more opportunity to burn fast; and this must be prevente by constant working. The central gutter in fig. 206 is somewha better, because it is not exposed to the direct action of the fire but all such gutters are with difficulty accessible, are too small to hold all the salt, too vulnerable by fire, and too liable to leakage from the necessity of employing angle-irons and many rivets. The latter must be countersunk so that the tools may not push against them.

The work in these pans is done thus. The salt is drawn with a rake towards the gutter; and when this is full, it is carefully scoope out by means of a perforated shovel bent to the sweep of the gutter The salt is put into a hopper, from which the drainings run bac into the pan. When it is half empty, more liquor is run in Usually the pan is filled twice in 24 hours and salt taken out fou times. The addition of liquor and the concentration are continu till the mother liquor contaminates the salt too much; this m

last from 8 to 24 days, according to the purity of the tank-liquor. The mother liquor then remaining is worked up separately in a similar way as for caustic soda.

Unless the crust forming on the surface of the liquor is constantly broken up, which requires much labour, the evaporation goes on very slowly; hence mechanical means are quite in their place here, as we shall see when describing Thelen's pan. It would no doubt be possible to place in the gutters a sieve bent to their shape, which would fill with salt, instead of this depositing on the pan-bottom itself; this sieve could be lifted out by means of chains and emptied. A similar arrangement the author has indicated in his treatise on Coal-tar (published in German, 1867, p. 148) for ammonium sulphate.

The principal drawback of the bottom-heat pans, the attaching of salt to their bottom, is avoided by the pan with mechanical shovels, constructed by Thelen (Chem. Industrie, 1878, p. 9), which is shown in figs. 207 to 210. Fig. 207 is a sectional elevation, fig. 209 a plan, fig. 208 a section on the line AB, fig. 210 a section on the line CD. Upon the cast-iron end plates of the semicircular pan the shaft W rests on two bearings and is moved by the worm E. The rods F are supported by stays and fixed to the main shaft; and to these a system of freely hanging, slanting shovels or scrapers G is attached. These, on passing through the liquor, touch the pan-bottom and move the salt towards the end. There are so many scrapers that no portion of the pan remains untouched on each revolution of the shaft. When the salt has arrived at the end of the pan, it is scooped out by a freely hanging shovel, whose sides are shaped to those of the pan, so that the salt cannot escape sideways. Four pans can be served by one fireman; the stirring-apparatus requires ¼ horsepower. When fed with previously heated liquor, each pan can turn out 18 to 20 cwt. soda-salt per 24 hours. A number of these pans are at work now in Germany, and, from all accounts, have fully answered their purpose.

An English patent of Mactear's (March 8, 1875) also prescribes stirring up the salt during evaporation; this is specially intended for separating it in a granulated state.

Many advantages over the flat-bottomed pans or those provided with gutters are offered by the *boat pans* invented by Gamble, and called so on account of their shape. The object is the accumulation of all the salt on the lowest part of the bottom, which is not touched

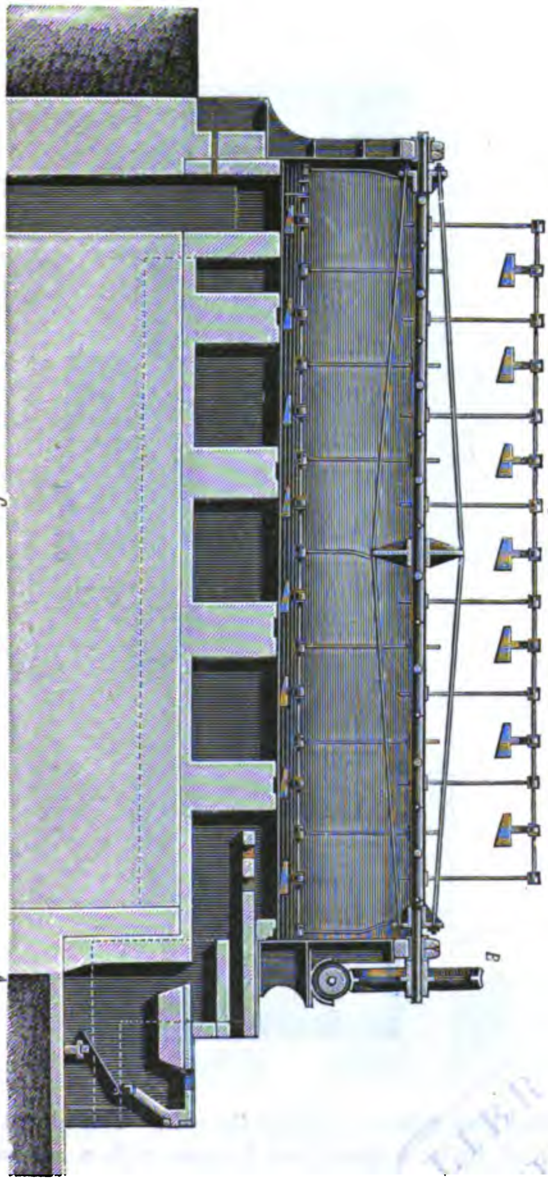


Fig. 207.

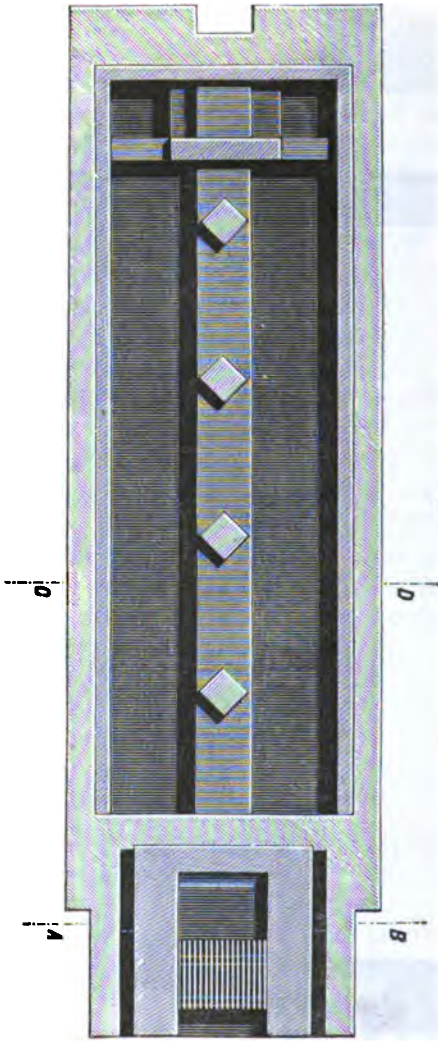


Fig. 209.

by the fire and thus cannot suffer by the salt. This object is much better attained by boat pans than by pans with a central gutter (fig. 206). The salt slides down by itself along the slanting sides of the pan, and on boiling is naturally deposited mostly in the

Fig. 208.

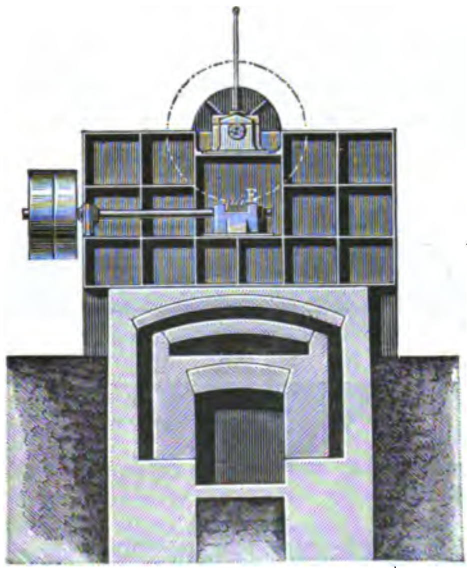
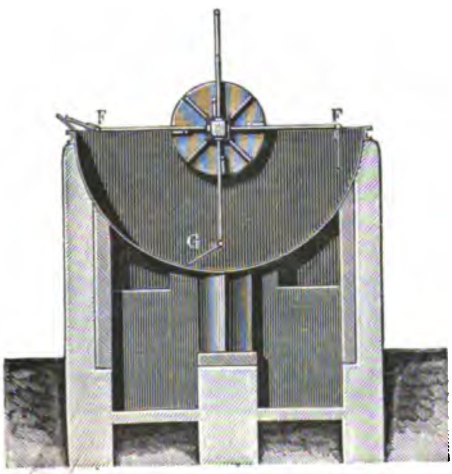


Fig. 210.



central part, which boils less strongly. Lastly, the construction of the pan is such that in it the drawbacks of angle-irons and rivets, mentioned in the case of gutters, are avoided. It is remarkable that, in spite of the advantages offered by the boat pans, and

although they are so common in England, they have made no way in Germany; the only intelligible reason for this is that flat-bottomed pans are more easily built and repaired than boat pans. These are made both of wrought and of cast iron, according to their especial destination. The former are shown in figs. 211 to 213, the latter in figs. 214 to 216. For boiling down tank-liquor for soda

Fig. 211.

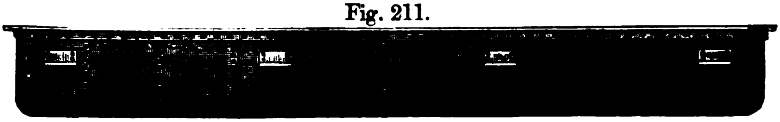


Fig. 212.

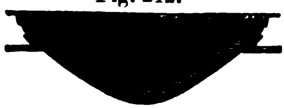


Fig. 213.

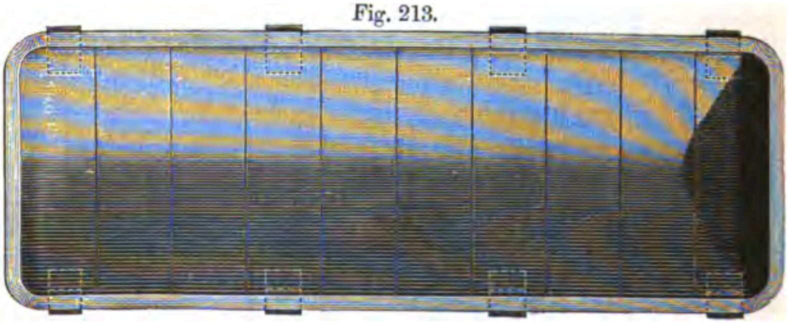


Fig. 214.

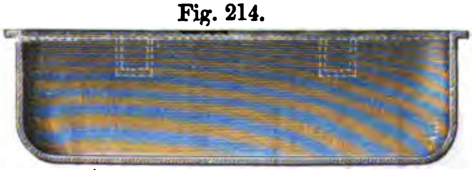


Fig. 215.

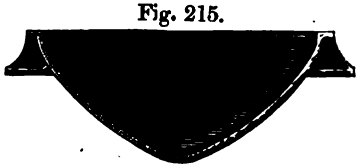
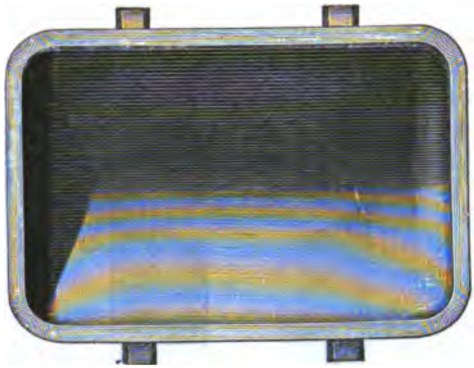


Fig. 216.

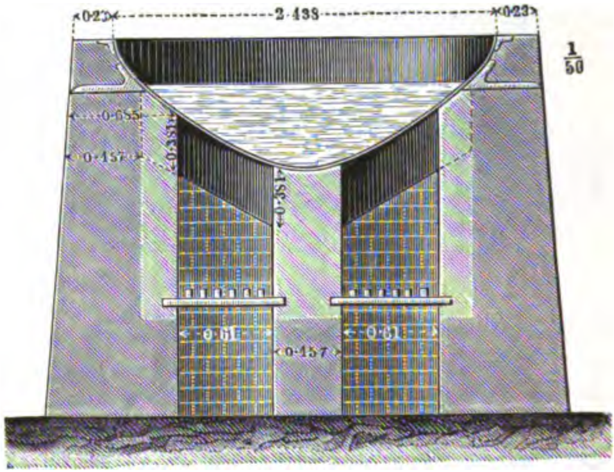


ash, wrought-iron pans are mostly employed, which can be made much larger, especially much longer, than cast-iron ones, and hence admit a better utilization of the fire. They are made of $\frac{3}{8}$-inch boiler-plate, with the following precautions. The plates of the bottom and the sides should have no longitudinal seams at all, or at most one such running along the middle of the bottom; the cross joints should be made with the lap of the plate which is nearer the fire downwards, so that the fire shall not play against the joint. Often, in order to avoid rivets, the whole portion of the pan above the fireplace for a length of 5 or 6 feet, and right across its width (that is, mostly above 10 feet), is made of *one* plate, which certainly can only be done at the Lowmoor or Bowling iron-works. A few brackets are riveted to the pan-sides to support it on the brickwork; an angle-iron running round the top serves both for this and for stiffening it. These pans can be made of any size; a very usual one is 25 feet long, 8 feet wide, and 2 feet 9 inches deep.

Although *cast-iron boat pans* (figs. 214 to 216) are usually employed only for caustic soda, we shall treat of them also here for the sake of simplicity. Their size is limited by the necessity of their being in one piece; the usual inside dimensions are 12 feet length, 8 feet width, and 3 feet 6 inches depth, with a thickness of 2 inches of metal. But few foundries can supply such large castings of the requisite quality; most pans come from Messrs. R. Daglish and Co., of St. Helens, and from the Widnes Foundry Company, of Widnes.

The *setting of the boat pans* is always done in the manner shown in fig. 217, not, as represented in former treatises, on pigeon-holed

Fig. 217.



arches, which consume too much fuel. There are two parallel fireplaces, each 2 feet wide and 4 feet long (sometimes a little longer); between these there is an 18-inch pillar, running along the whole length of the pan, carrying its bottom and keeping the fire off the same. The back wall of the fireplace slants upwards, parallel with the pan-bottom, at a distance of 15 inches from the same; and the brickwork is continued in the same way along the whole pan; so that two flues of 15 inches height are formed, which, however, rise a little higher up than in the fireplace, viz. to a width of 3 feet 3 inches, measured along the pan-bottom. The liquor must stand at least up to this height, as shown in the figure. Behind the pan the flues unite again before entering the chimney. The flame very often (in the case of short cast-iron pans regularly) first travels underneath another boat-pan, set in the same way. Frequently three or four projections of 6 inches height are made on the bottom of the flues, also running parallel with the slanting pan-bottom, and consequently only 9 inches distant from it; these saddles are to force the flame closer to the pan.

Those boat-pans which are heated by the waste fire of a black-

ash furnace are set just as shown here, except that there are no fireplaces.

Sometimes, whilst the pan is mounted on three longitudinal pillars as hitherto shown, the fireplaces are built against them in front as a continuation of the two flues; and in that case of course they are arched over: each of them then has a grate of 2 feet 9 inches width and 4 feet 6 inches length.

Boat pans are always employed for "fishing," which is much more easily done in them than in the top-fired fishing-pans previously described. In England mostly no vapour-hoods are fixed over them, but the steam is drawn off by ventilation from above.

The salt is fished out from these pans in a degree differing according to the strength of soda-ash to be obtained, liquor being fed in from time to time. When the point has been reached where the fished-out salt ceases to be pure enough, the red liquor is either boiled down to dryness for "caustic ash," or worked up for caustic soda (as we shall see afterwards), or carbonated by carbonic acid (as is explained at the end of this Chapter).

The average specific gravity of the *red liquor* from these pans is 1·315. For boiling them down to dryness, in Lancashire a furnace with a dished bed is sometimes used, the working-door of which is tightly shut. In this the red liquor, mostly with the addition of a little tank-liquor, is boiled down to the consistency of mortar. Now the door is taken away, and the charge finished as in an ordinary calcining-furnace. In this way "caustic ash" containing about 50 per cent. Na_2O, 8 or 10 of which are present as $NaOH$, is obtained. This English caustic ash, however, is much inferior to that made in France (p. 496), being of a very dirty colour and uneven grain.

A more systematic separation of the different products is (or was in 1862, according to Hofmann's 'Report by the Juries,' p. 27) carried out by Kuhlmann. In a pan, at the sides of which the respective heights are marked, the original tank-liquor of specific gravity 1·286 is first evaporated to seven twelfths of its volume, and the salt precipitated in the meantime fished out. This yields a very pure ash containing 96 per cent. Na_2CO_3. By boiling down the mother liquor to three sevenths of its volume and fishing out the salt, a product is obtained testing 85 per cent. Na_2CO_3. The residue, dried down in a furnace, yields a very caustic ash, charged with all the soluble impurities of the liquor.

More accurate experiments on this subject have been made by Kolb (Ann. Chim. Phys. x. p. 106). According to him the several salts are not precipitated exactly in the succession corresponding to their degrees of solubility, because when occurring together in a liquor they influence the solubility of one another. When, *e. g.* a liquor *a* was concentrated up to the first separation of salt, and then samples of the salts were taken at seven different degrees of concentration (assuming that the volume of the liquor at the point at which the first separation of salt began was = 100), they showed the following composition :—

	Liquor *a* = 100 vols.	Residual volume of the liquor *a* at the time of taking the samples, per cent.						
		27	24	20	15	10	5	2·5
Sodium carbonate ...	81·6	88·2	90·4	88·8	85·2	71·3	67·1	43·3
„ hydrate	8·2	2·9	4·0	5·7	8·0	10·6	14·3	27·7
„ sulphide	0·1	trace.	trace.	trace.	trace.	0·01	0·35	1·3
„ chloride	5·9	2·8	2·6	2·7	4·3	6·4	9·3	20·3
„ sulphate	4·3	1·4	1·5	1·4	2·5	9·8	6·8	2·6
Silica and alumina	1·2	4·2	0·9	0·8	0·6	1·2	1·1	4·6
Iron sulphide		trace.	trace.	trace.	trace.	trace.	0·1	0·2
	101·3	99·5	99·4	99·4	100·6	99·3	99·0	100·0

The salt in the last column is quite impure red mother-salt.

From the above analyses the following rules can be deduced. In liquors containing, along with sodium carbonate as principal constituent, caustic, chloride, and sulphate, on increasing the concentration, first the last-named will increase together with the carbonate; the chloride will remain in the liquor almost to the very last. The more caustic a liquor, the more perfectly the sulphate and chloride are separated; and the caustic accumulating in the liquor ultimately causes an almost perfect separation of all other salts. [This fact has long been recognized in manufacturing

caustic soda, as we shall see later on.] If the fished-out salts be more specially considered, the precipitation of the carbonate, which in the beginning is influenced by the sulphate, describes an ascending curve, long remaining stationary if only little sulphate was present; the curve soon drops quickly when the chloride and caustic begin to act. When the soda has been made from sulphate containing very little chloride, the salts first fished are poorer in carbonate than the following ones. If, however, the sulphate (and consequently the tank-liquor) contained much chloride, the salts first separated are richest in carbonate; afterwards the percentage decreases until all NaCl has been separated by the caustic, whereupon the original percentage of soda is reached again. If, lastly, the liquor is rich both in sulphate and chloride, the percentage of soda, initially low, is raised by the elimination of the sulphate, remains stationary for a short time, and then again is lowered by the influence of the chloride.

The following Table (from Payen's 'Précis,' 1877, i. p. 468) gives an idea of the composition of the successively separated salts after calcining:—

	1.	2.	3.	4.	5.	6.
Alkalimetrical titre, according to Decroizilles	92	89·5	82·5	78·2	60·5	74
Caustic titre, ditto	1	2	10	17·2	30·00	73
German alkalimetr. degrees (% of Na_2CO_3)	99·5	96·8	89·25	84·6	65·5	80·0
Na_2CO_3	98·20	94·60	77·42	70·61	33·00	1·16
NaOH	0·80	1·60	8·16	14·03	24·50	29·10
Na_2SO_4	0·50	0·80	7·15	8·06	3·30	1·00
NaCl	0·50	9·90	7·10	7·10	33·30	11·07
Fe, SiO_2, Al_2O_3, oxidizable sulphur	...	0·05	0·17	0·21	5·90	1·04
Insoluble	...	2·05	...	...	...	...
Water	...	...	...	...	...	56·3

The salts 1 and 2 give an ash of 90° Decr.; 3 and 4, one of 84 or 85 down to 80°; 5, a weak caustic ash; 6 is the red liquor.

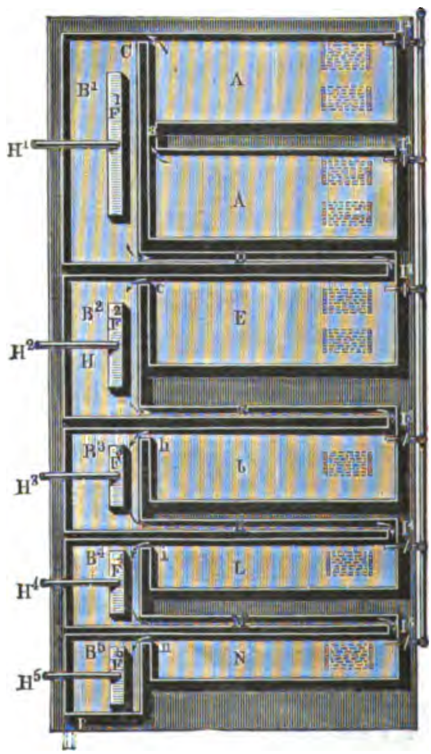
Other Concentrating Apparatus.

These have found very little application in alkali-manufacturing, ingeniously constructed as some of them are. We point out especially the wire-rope tower of Ungerer, which will be described in treating of the carbonation of the liquors.

A proposal has been patented by Kneller (Dec. 22, 1842) for injecting steam or hot air by a system of pipes through the liquor-pan, in order to preserve the pan and to obtain a purer salt than by employing top heat.

A very ingenious, but too complicated, apparatus was patented by Gossage (June 15 and Oct. 4, 1853). As his principle seems good, we give the following short description. In fig. 218 all the

Fig. 218.



pans are to be understood as on a level. A A are heated directly either by special fires or by the waste heat of a furnace. They communicate with each other by the channel *a*, and with the "cooling-pan" B^1 by the channel C. B^1 communicates with the heating-pan E by the channel D, and E with the cooling-pan B^2 by the channel *c*, and so forth through the whole series. Each cooling-pan, B^1, B^2, &c., has a vessel F^1, F^2, &c., for dividing into many bubbles a current of air blown in through the pipes H^1, H^2, &c. by means of an air-pump. I^1, I^2, &c. are cocks connected with a liquor-tank. Each of the heating-pans A A up to N is fed with liquor; and when this has been concentrated so far that on cooling down a few degrees it would separate salts, more liquor is run in, so that the hot concentrated liquor flows over through C into B^1, where its cooling is promoted by blowing in a stream of air, which also favours evaporation. Here salt is deposited, whilst the mother liquor flows through D into the heating-pan E, where it is again heated and concentrated, flows over into the cooling-pan B^2, and so forth, till the last mother liquor runs away through P. By means of the cocks I^1, I^2, &c., as much fresh liquor is run into each of the heating-pans as prevents the overflowing hot concentrated liquor from depositing the salt instantly, but not after a small amount of cooling. If liquor free from Na_2S (and consequently from FeS) is employed, the salt deposited in B^1 yields very pure soda ash. That in B^2 contains already, along with carbonate, caustic and ferrocyanide in sensible quantities; it is put into B^1, where it is almost completely cleared of these impurities. The latter are found in gradually increasing quantity in each successive cooling-pan; and the salts are moved from pan to pan until they ultimately get into B^1. Thus in B^1 a nearly pure carbonate will be accumulated; from B^5, on the other hand, a liquor containing very much caustic and ferrocyanide will run out, which is treated as will be described directly. We will first mention that Gossage enumerates the following improvements:—heating the air injected into the liquid, to promote evaporation; placing a paddle-wheel in the channel between the two pans to ensure the circulation of the liquid, &c. The last mother liquor, along with the liquor obtained by washing the pure alkali with water or (according to Ralston) with a concentrated solution of pure soda, are to be causticized completely by lime, and the ferrocyanide obtained from them by crystallization.

Of course boiling-down pans might be heated by any other waste heat than that of a ball-furnace. We will only mention that now and then the gases from coke-ovens and blast-furnaces have been used for this purpose, viz. at Wallsend and Walker-on-Tyne.

A patent taken out by J. Dale (Feb. 24, 1859) makes use of the latent heat of steam by carrying the steam from a pan, closed for this purpose, through a coil of piping into the liquor contained in a second pan, and the steam given off in this into a third pan, the pressure of course decreasing in each consecutive pan. This process was actually used at Washington for concentrating weak caustic liquors, but has not made its way elsewhere into alkali-works, because there are great practical difficulties, the apparatus needing incessant repairs, &c. The same principle is used in all beet-root-sugar works; but there the liquors do not act upon metals and deposit salts, at any rate at that stage.

Another concentrating apparatus, patented by Stevenson and Williamson on July 2nd, 1856, is at work only in the factory of its inventors at South Shields; but it yields very good results for the purest alkali. The following is a short description of it:—Fig. 219 shows an elevation, fig. 220 a top view, fig. 221 a section of this apparatus, which is intended to heat the pan only by fire applied at the sides, not at the bottom, and to prevent any incrustation of salt on the heating-surface. A is a cylindrical pan, ending at the top in a truncated cone; it is heated by the fireplace B or some waste heat, the flame travelling in a flue C round the largest part of the vessel. In the centre there is a vertical axis E to which arms F F are fixed, which nearly reach to the side of the pan. The gearing GH and the fast-and-loose pulley J serve for moving the axes with its stirring-arms, which prevent any salt from incrusting the side of the pan. Between the fireplace B and the end of the flue C there is an opening D in the pan, beginning below the level of the liquor and forming a communication with the settling-vessel K. The salts pass through D into K, where they subside, are lifted by the elevator L, and deposited in a drainer M with a finely perforated bottom from which the mother liquor always runs back into the pan. O is the pulley for moving the elevator. The top part P with the pipe Q serve for carrying away the steam; R is the feed-pipe with its cock.

Fig. 219.

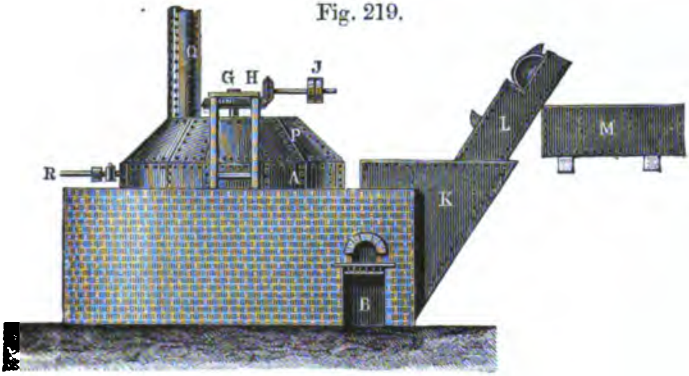


Fig. 220.

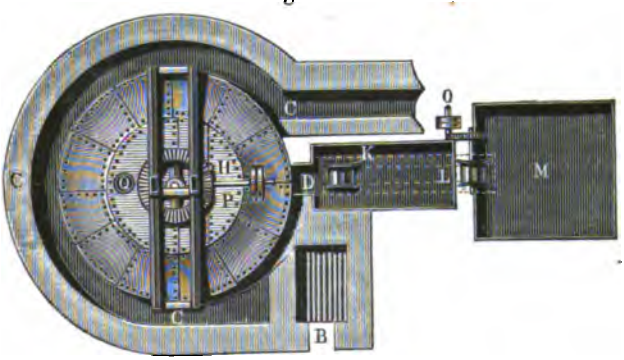
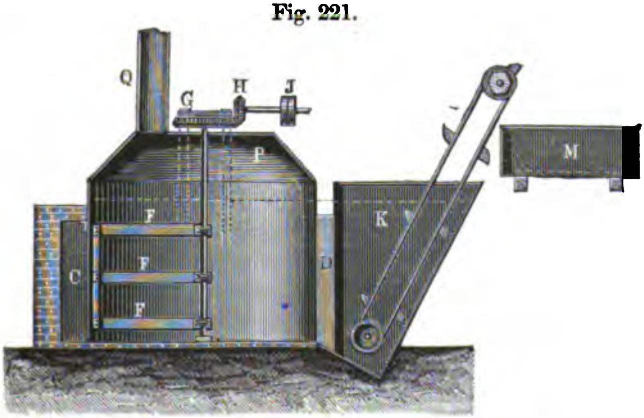


Fig. 221.



Carbonating and Oxidizing the Liquors.

In most English works the settled tank-liquor is boiled down as it is; and along with the pretty pure sodium carbonate ($Na_2CO_3+H_2O$) which separates, a very caustic mother liquor, the *red liquor*, is obtained, which contains very much caustic with a good deal of sulphide and of the minor impurities of the tank-liquor. Wherever the red liquor is worked up for caustic, it is in any case separated as much as possible from the salt, and the latter calcined by itself, which is done without any difficulty. But where no caustic is made, and no red liquor can be kept separate, the caustic and sulphide must be removed by the process of *carbonating*. On the Tyne this is always done by putting sawdust in the pans, which on calcining burns and gives off carbonic acid, the latter converting the larger portion, but never the whole, of the caustic into carbonate; the sulphide and the intermediary oxides of sulphur, such as sulphite and hyposulphite, pass over to a very small extent into carbonate, the largest portion into sulphate.

The process of carbonating with sawdust in the furnace is difficult; and in the *best* case the ash still retains 1 per cent., but more usually 2 per cent. Na_2O in the state of $NaOH$. Nearly all the Na_2S is lost, as it is converted into sulphate, which is not paid for in the price of soda ash. Lastly, in this process the FeS dissolved by means of Na_2S in the liquor is not removed, but, on calcining, converted into ferric oxide, which stains the ash yellow.

A much more rational process is *carbonating with carbonic acid*. To some extent a transition to this process is that of *oxidizing by air*, which also serves for other purposes, and which was introduced by Gossage (patent May 18th, 1853). We shall describe this first, as it can be applied to the treatment of tank-liquors for ash, although it is usually employed for caustic (oxidation by means of chloride of lime or nitrate of soda is probably exclusively used for producing caustic, not for carbonate). For this purpose an iron tower, filled with coke or any other suitable material, is employed, on the top of which the liquor is pumped, divided by some contrivance into many jets, and run down. The top of the tower is connected with a good chimney; or a draught is produced in it by means of a jet of steam. Round its bottom a large number of holes are made; through these a continuous current of air is aspirated, which on coming into contact with the liquor finely divided by the coke, gradually oxidizes the sulphide to sulphite and ultimately to sul-

phate, precipitating the FeS in an insoluble form. The liquors should be about 42° to 50° Tw., and should be employed hot. Usually the oxidation is not perfect by one passage through the tower, and the liquor must be pumped up and run down again, sometimes repeatedly, till it has become quite colourless and gives no reaction upon sulphides with lead paper. Now the liquor is allowed to settle; the FeS &c. are deposited, and the clear part conveyed away for evaporation &c. Thus the iron is kept out of the soda and this obtained of a much whiter colour. A tower of 30 feet height and 8 feet diameter is said to suffice for a weekly make of 50 tons.

The application of Gossage's coke-tower, which serves both for oxidizing and carbonating, has several drawbacks. As it can only be made of moderate height, the liquors must be pumped up several times, at the cost of much labour and some mechanical loss of soda. Also the packing of the tower, be it coke or any other material, absorbs much soda, which cannot easily be recovered. The loss from these sources is estimated at 2 or 3 per cent. of the total soda. [The application of wire ropes or chains on Ungerer's principle (see below) would no doubt overcome this.] Hence in many works Gossage's oxidizing towers have been replaced by Hargreaves's apparatus (Chem. News, xiii. p. 265), which in the manufacture of caustic is also intended to do away with bleaching-powder and nitrate of soda. It is shown in figs. 222 and 223 as actually employed.

Fig. 222.

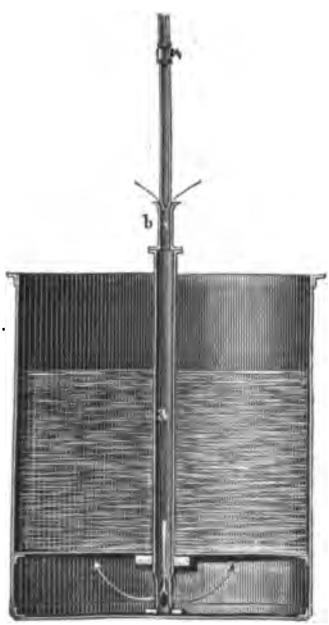


Fig. 223.

It is a cylinder of ⅜-inch boiler-plate, 6 feet wide, 7 feet high, open at the top, with a perforated false bottom 15 inches above the true bottom, filled with liquor up to three quarters of its height. In the centre a 4-inch pipe *a* passes through the false bottom and has below this four large lateral holes; above the cylinder a lead pipe *b* of half the width is attached to it, which at the top is widened out a little. A steam jet from a 1½-inch pipe *c* enters into it centrally; and the steam (of about 45 lb. pressure), on rushing through *b* and *c* into the liquor, forces air along with it through the funnel of *b*, and the more so as it is soon condensed in the cold pipe. The air escaping through the lateral openings of *a*, is by the holes of the false bottom divided into many jets, and causes the liquid to bubble violently; the intimate and manifold contact into which it comes with the air, together with the heating caused by the steam, bring about the oxidation of the sulphide. With an apparatus of the above dimensions, and 45 lb. steam-pressure, it takes from 3 to 5 hours to oxidize the liquor so far that it ceases to give any black colour with lead paper. The Na_2S is then completely oxidized, and the FeS precipitated; but there are still sulphites and hyposulphites present, which are oxidized on calcining. Hargreaves's apparatus is nothing but an imperfect kind of injector; it consumes very much steam for a comparatively small amount of work, with corresponding dilution of the liquor, and is most advantageously replaced by the rationally constructed Koerting injectors.

Much more efficient than treatment with air only is that with *carbonic acid* only (patented by Shanks, on May 27th, 1841), or with *air and carbonic acid together*. Already in 1838 Beringer had proposed the treatment of red liquors by carbonic acid (Pharmaceut. Centralhalle, 1838, p. 559), and recommended the employment of lime-kiln gases for this purpose; but this idea was first practically carried out in England. By it, in the first place the caustic is converted into carbonate (which in the oxidizing treatment is done very imperfectly by the small amount of CO_2 contained in the air); the Na_2S is decomposed, and at least a good portion of it converted, not into sulphate, but into carbonate, and is thus obtained in an available form. Thirdly, the sodium aluminate and silicate are also decomposed. In this operation, according to Stroof (Wagner's Jahresb. 1872, p. 259), from red liquor a salt of the formula $2Na_2SiO_3 + Al_4Si_3O_{12} + 6H_2O$ is separated; on evaporation to 52° Tw. [but this is only the strength of fresh tank-liquor?] another

salt, $2Na_2SiO_3 + 2Al_2SiO_5 + 3H_2O$ is obtained. Scheurer-Kestner found that by the action of CO_2 on tank-liquor an aluminium silicate was separated having the composition 32·32 SiO_2, 43·45 Al_2O_3, 23·93 $H_2O = Al_4Si_3O_{12} + 6\ H_2O$ (Rép. Chim. Appl. iii. p. 446).

The ash is much whiter when made by this process than otherwise. The treatment with CO_2 is more rarely applied to tank-liquors as a whole, than to red liquors if these are not to be worked up for caustic. Shanks had proposed to apply it to the black ash broken into pieces and moistened in closed vessels; but himself preferred the application of coke- or pebble-towers. Where at the same works caustic is made from tank-liquor by means of lime, the CO_2 escaping on burning the lime is the simplest and cheapest source for it. (Carbonic acid made from HCl and $CaCO_3$ nowadays only pays in a few places where much weak acid is run to waste.) The top of the lime-kiln is connected by a flue with the coke-tower placed at a higher level; or an air-pump is put in between, which is dearer and necessitates cooling the gas. Hargreaves's apparatus can be employed here as well, especially when a Koerting's injector is adopted, which is made for aspirating other gases than air. According to Stott's patent of Nov. 27, 1855, the CO_2 is to be pumped in under pressure. Usually iron cylinders of 20 to 40 feet height and about 5 feet wide are employed, standing in a saucer forming a water-lute; the impure CO_2 gas enters at the bottom and escapes at the top; the liquor is run down continuously or at intervals by some distributing arrangement. In the place of coke, earthenware cylinders or pots are sometimes employed, which permit the recovery of a portion of the adhering crusts of salts, very difficult with coke.

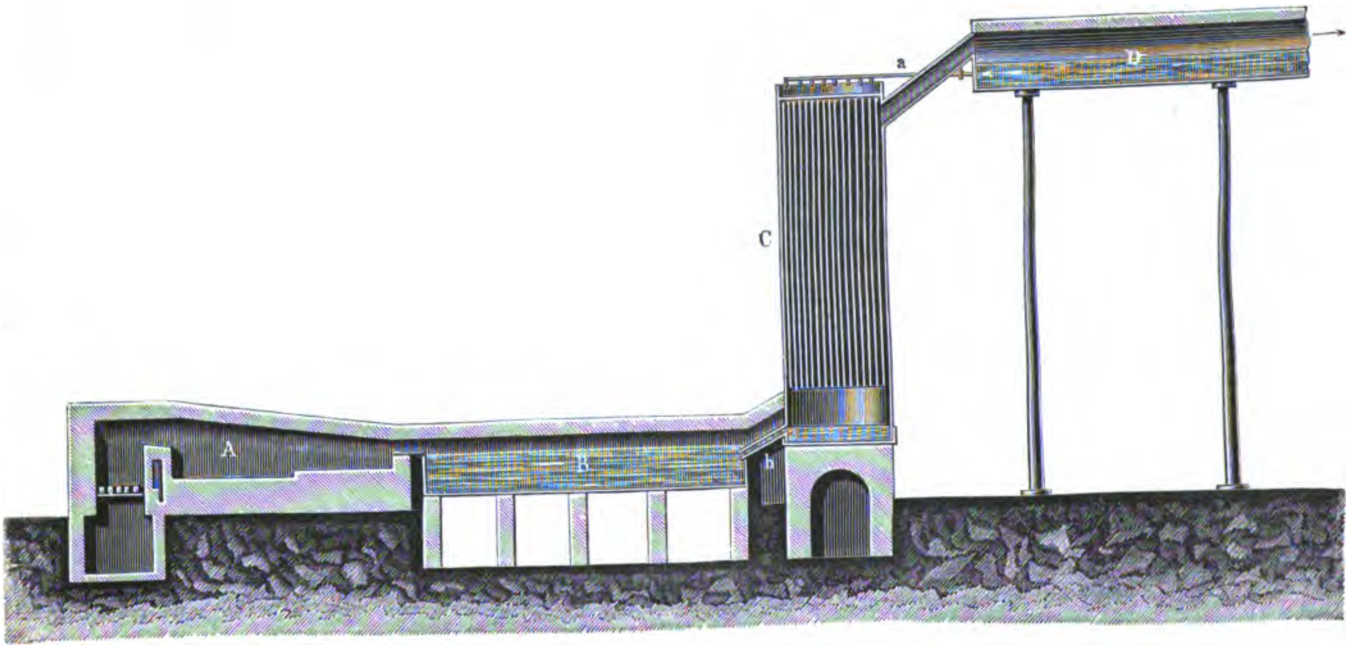
A very perfect carbonating apparatus is found at the Ludwigshafen works. There are three iron cylinders about 6 feet wide and 12 feet high, without any coke packing &c., filled with liquor. The gases of a lime-kiln are pumped by a strong air-pump alternately into one or the other of the cylinders first; and from this they pass into the second cylinder, and sometimes from that into the third. The liquor is in each cylinder treated first with the partially spent, then with the strong gas, till it is completely carbonated; by admitting a little steam the action is hastened and is finished in 2 or 3 hours. Then the liquor is forced into settlers by means of an ordinary air-pump and a delivery-pipe, the cylinder itself serving as a forcing-vessel.

The simplest kind of carbonating is that with *fire-gases*, which can be combined in a very rational way with the concentration; but the soda ash is not quite so white as with the application of pure gas entirely free from smoke and coal-ashes. For this purpose, behind the boiling-down pan (which may be heated from top or bottom) a tower is erected, in which the settled tank-liquor is run down, and from which it goes directly into the pans. The fire-gases from the black-ash furnaces, having previously heated the pans, pass through the tower, and from its top to the chimney; this might be effected by means of a horizontal flue made of iron at the bottom (say an old steam-boiler cut in two) and arched over at the top, serving at the same time as settler and store-tank for the liquor. The sketch, fig. 224, will make this clear. A denotes the furnace, B the pan, C the tower (fitted with chains or wire-ropes stretched by weights or by screwing down), D the half of an old boiler, arched over, or some other flue leading to the chimney. In such an apparatus the tank-liquor would first be pumped into the flue D, serving as a settler; from this it would run, divided into many jets by means of the pipe *a*, through the tower C; and as on its way it met the carbonic acid and oxygen of the fire-gas, it would be oxidized and carbonated by the latter, also utilizing the heat to the utmost. It then runs by the pipe *b* into the pan B, where it is finished. The fire-gases travel the opposite way to the liquor.

The inner fitting-up of the tower is very important here. It might be filled with coke, broken pots, &c.; but this is not preferable, because it would cause a loss of soda, and if the tower were empty at any time the coke might even take fire. The tower would have to be very high indeed for completely purifying the liquor, as the action of the gases is not very quick; and it would not be very practicable to place such a tower behind a black-ash furnace, owing to the check it would give to the draught; so that some other source of fire-gases would have to be employed.

Another arrangement might be given to the tower by fixing a number of horizontal or slightly inclined shelves within it, leaving alternately at one side or the other a sufficiently wide space for the passage of the fire-gases, so that they would be compelled to ascend in a zigzag course and meet the liquor running down in a thin jet (similar to the absorption-tower for nitrous gas or hydrochloric acid shown in fig. 160, Vol. I. p. 378). This apparatus, recommended by

Fig. 224.



Gossage for concentrating, has the disadvantage when used for that purpose that the salt adheres to the plates and is difficult to get off; hence it should not go so far as to deposit any salt. This might be more easily avoided *behind* the concentrating-pans, where the gases are much cooled down; neither would the reproach of checking the draughts be so deserved here as with a coke-tower &c.; but the contact between liquor and fire-gas is too slight, and the oxidizing and carbonating action too slow. In any case, on account of the precipitates of iron sulphide and aluminium silicate (p. 518), the tower would require to be frequently cleaned out, an operation not very easy to perform.

By far the most perfect apparatus for this purpose is that patented by Ungerer on Oct. 10th, 1872, which, though only destined by the inventor for concentrating liquids by hot air, at the same time performs the oxidizing and carbonating function better than any other apparatus. It consists of an iron tower, or a brick tower lined with sheet iron, the top of which consists of an iron pan with perforated bottom. From this several hundred wire ropes hang down and are kept perpendicular by a stretching arrangement at the bottom. In this tower the fire-gases ascend; the liquor runs down upon the wire ropes, and that in a spiral course, following the twist of the rope, thus being exposed to the action of the gases on an immensely extended surface; the evaporating, oxidizing, and carbonating action of the gases is thus utilized to the utmost without materially interfering with the draught, if the tower is wide enough, as the gases only ascend vertically. Even a separation of salts does no harm, because they can be made to come off by shaking the ropes. In the place of wire ropes, chains may be employed, which can be cheaply bought when rejected for lifting; a stretching arrangement can then be dispensed with. Ungerer's apparatus will also be most advantageously employed for carbonating by means of carbonic acid taken from a lime-kiln or made by means of hydrochloric acid.

The most recent and probably the most efficient plan for removing the sodium sulphide, and with it most of the iron, from tank-liquor is that patented by Pauli (April 2nd and 18th, 1879, Nos. 1306 and 1530). To the liquor a very small quantity of powdered dioxide of manganese is added, or, preferably, of washed Weldon mud, *i. e.* recovered manganese (comp. Book IV. Chap. VI.); and air and steam are injected by means of a Koerting's blower. The Na_2S is oxi-

dized by the MnO_2; and the latter is continually regenerated by the air, thus acting as a carrier of oxygen to the Na_2S. In this way the oxidation of Na_2S takes place with extraordinary rapidity and completeness. When it is finished, the liquor is allowed to settle: the manganese sinks to the bottom; the supernatant solution is drawn off; and fresh tank-liquor is run in. The MnO_2 by itself would serve an infinite number of times; but since ferric oxide, silica, alumina, &c. are precipitated from the tank-liquor as well, the precipitate gradually becomes so bulky that it must be removed from time to time and fresh manganese added. The newest patent in this branch, Parnell's, No. 4188, Oct. 21, 1878, employs metallic zinc or a solution of zinc oxide in caustic soda for desulphurizing the liquors. Similar plans, frequently tried before, have always failed to give satisfactory results.

Calcining the Black Salt (Finishing the Soda Ash).

We have pursued the tank-liquor till it has attained its fullest concentration in the pans and the "black salt" has been separated from it. In a few cases we have already described its conversion into finished ash, where evaporation and calcining go on in the same furnace and cannot be separated in the description. Formerly this was the general process; but in the modern style of alkali-making the two operations are kept apart in most cases. We shall now describe the second of them, viz. the calcination of the black salt.

This operation presents very different degrees of difficulty, according to the quality of the black salt. It takes place most easily with a pure salt of high strength, almost or entirely free from caustic and sulphide. Such a salt is that fished from pans fired from underneath, whether flat-bottomed or boat pans, during the first period of evaporation, or that obtained from carbonated liquors. Here only the mechanically adhering water and the one molecule of it chemically combined with Na_2CO_3 has to be removed by the heat of a reverberatory furnace; and ultimately the mass has to be brought to a red heat in order to destroy any organic substances present and to oxidize the remaining sodium sulphide. The mass of course must be turned over now and then, and the lumps crushed; but with a properly constructed furnace, as no sensible quantities of caustic &c. are present, no fluxing need be apprehended, even at

a bright red heat; and therefore pretty large furnaces and quantities of salt may be employed.

These furnaces are always of the reverberatory kind; the grate is always much smaller in comparison with the bed than that of a black-ash furnace. The best kind is that fired by gaseous fuel, which will be described further on. The fire-bridge is always very high, and leaves but a narrow slit between itself and the arch; so that the ashes are kept back as much as possible, and the flame is compelled to travel more along the furnace-roof, and to act by radiant heat.

Formerly the furnace-bed was frequently made of metal plates (comp. p. 497); now it is usually made of fire-bricks set edgewise.

By calcining fished salts, soda ash of from 52·5 to 57 per cent. Na_2O, according to circumstances, can be made. In England the latter strength is only obtained from revolving ball-furnaces, on the Continent (with slower and more careful work) from hand-furnaces as well, at any rate by steaming the salt (p. 495). The soda ash is either ground and sold as such, or sometimes, as we shall see, refined.

The operation with *caustic salt* is very different, whether it contains much sulphide or not. Here the danger of fluxing during the calcining is very great; and this must be carefully avoided, because it would render the product nearly useless. Only just so much heat must be employed as will dry the salt; real calcination cannot take place. In Lancashire the caustic fishings from red liquors are calcined in this way:—First a small quantity of ordinary, not caustic, salt is calcined; when this has become red hot and ready for drawing out, it is spread on the furnace-bed and, according to the desired strength of the salt, three or four barrowfuls of fishings are thrown on the top of it, quickly spread with a rake, worked through a few minutes with the hot finished charge, and drawn out. The product (which goes into the trade as "caustic ash") has not a bad colour, but contains only from 46 to 50 per cent. Na_2O, according to the quantity of the salt; of the above, from 5 to 8 per cent. are present in the caustic form (comp. also pp. 496 and 509).

When caustic ash is not made from the very impure red-liquor fishings, but from the entire tank-liquor, it cannot be dried in an ordinary calcining- or finishing-furnace, but with all care and at a very low heat. By leaving out the sawdust the salt remains

very caustic, but sometimes contains 52 or even 54 per cent. available soda, and appears nearly white even after cooling.

Caustic soda is difficult to grind, and hence is mostly sold unground; in France it is granulated by the process described in p. 498.

The calcining is much less difficult if, as is generally done on the Tyne and also in some English works elsewhere, sawdust has been added to the liquor in boiling down in order to convert the sulphide and caustic into carbonate. Hence the calcining process is directly described as *carbonating*. A furnace actually serving for this purpose is represented in figs. 225 to 228. Fig. 225 is a horizontal

Fig. 225.

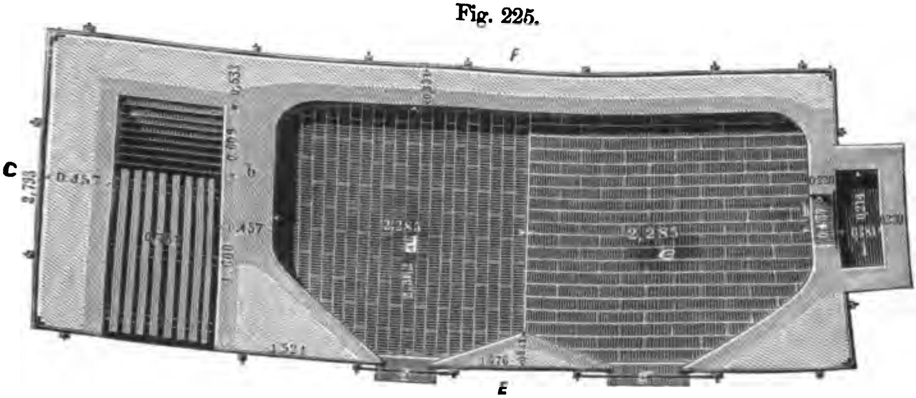
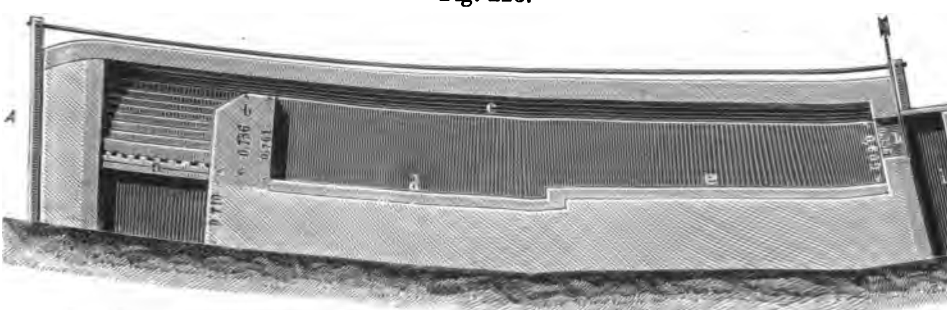


Fig. 226.



section along the line A B of the sectional elevation fig. 226 is taken along the line C D of the plan; fig. 227 is a fron

Fig. 227.

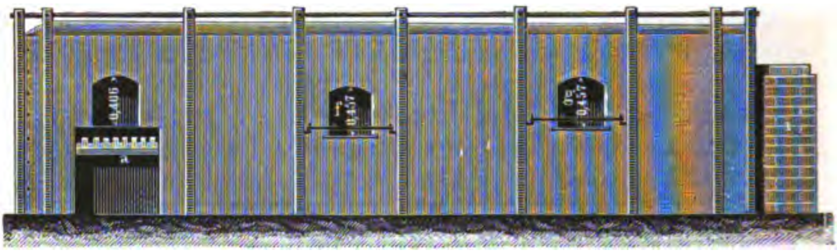
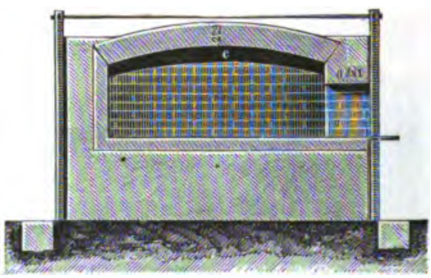


Fig. 228.



tion; fig. 228, a section along the line E F of the plan. The grate, *a*, in this case does not absolutely need an ash-cave (comp. p. 386), because the fire is not so strong; but such a cave is always preferable on account of better cleaning the fire. The fire-bridge *b* requires no bridge-plate nor air-course, as the charge does not get up to the fusing-point. It is very high and crescent-shaped at the top, but somewhat flatter than the arch, so that the slit *c* is only 4 inches high at the sides, 6 inches in the centre. The furnace has two beds, *d* and *e*, made of fire-bricks on edge; the drawing shows the way in which they are set. They are put in without mortar, just as was described in the case of the black-ash furnace, p. 387. The back bed, *e*, is 3 inches higher than the front bed, *d*. The arch is less sloped than in the black-ash furnace; its abutment at the back end is still 2 feet above the furnace-bed. The snore-hole *h*, leading to the flue *i* and provided with a damper, is just below the arch. This, again, acts so that the flame is not drawn down so much upon the charge as it is purposely in other cases. These furnaces are usually cased in metal plates, which is not absolutely ne-

cessary, but makes them last much longer and keeps the heat well together; once set, they last almost for ever.

Of course the whole must be bound by uprights and tie-rods. A well-built carbonating furnace requires very few repairs, except lining the fireplaces from time to time.

The fireplace shown in the drawing is evidently not a rational one; it should be adapted to the fuel. Carbonating-furnaces are best heated with gaseous fuel, because then coal-ashes are kept out and soot can be avoided as well; the flame and the air can be regulated to a nicety. In Germany, and here and there in France and England, this plan is followed. A very successful gas-generator, actually in operation at the Aussig works, is represented in figs. 229 to 232; similar fireplaces may be attached to black-ash fur-

Fig. 229.

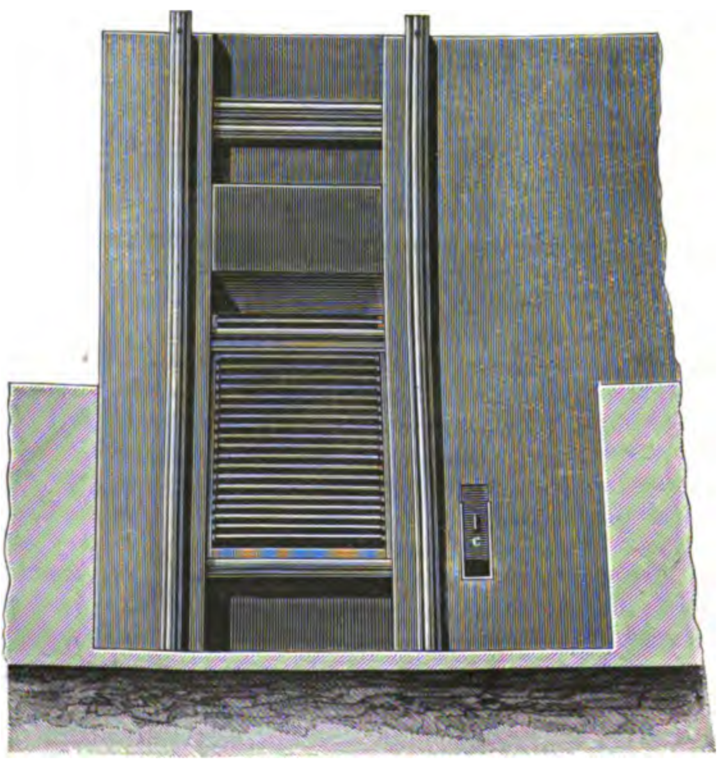
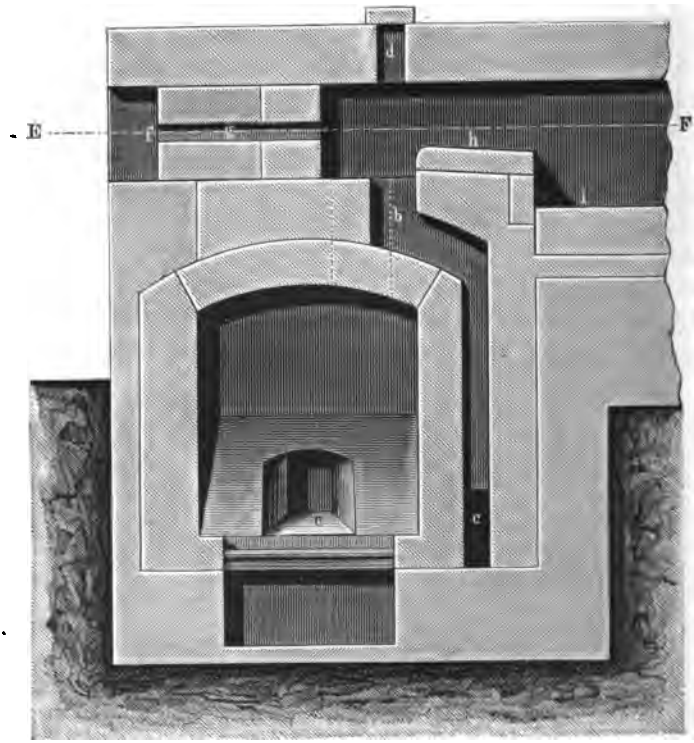


Fig. 230.



naces, decomposing-furnaces, platinum stills, steam-boilers, &c. *a* are the gas-slits; *b*, air openings; *c*, regulation of the air; *d*, openings for cleaning the gas-slits; *e*, opening for pulling out the scars; *f*, mica plates; *g*, peep-holes; *h*, fire-bridge; *i*, furnace-bed. The plates from *x* to *y* are usually plastered up with clay, and might be left out as unnecessary.

The work in the carbonating-furnace may be divided into three stages—drying, carbonating proper or cleaning, and firing. The drying principally takes place on the bed *e* (fig. 226), whilst a former batch is already on *d*; but it must be continued even after the batch has been pulled down from *e* onto *d*. Usually each bed holds enough salt to yield 15 or 17 cwt. of soda ash; and it takes from 5 to 5½ hours to finish a batch; so that a furnace turns out from 3 tons to 3 tons 8 cwt. of ash per 24 hours; it consumes 24 cwt. of

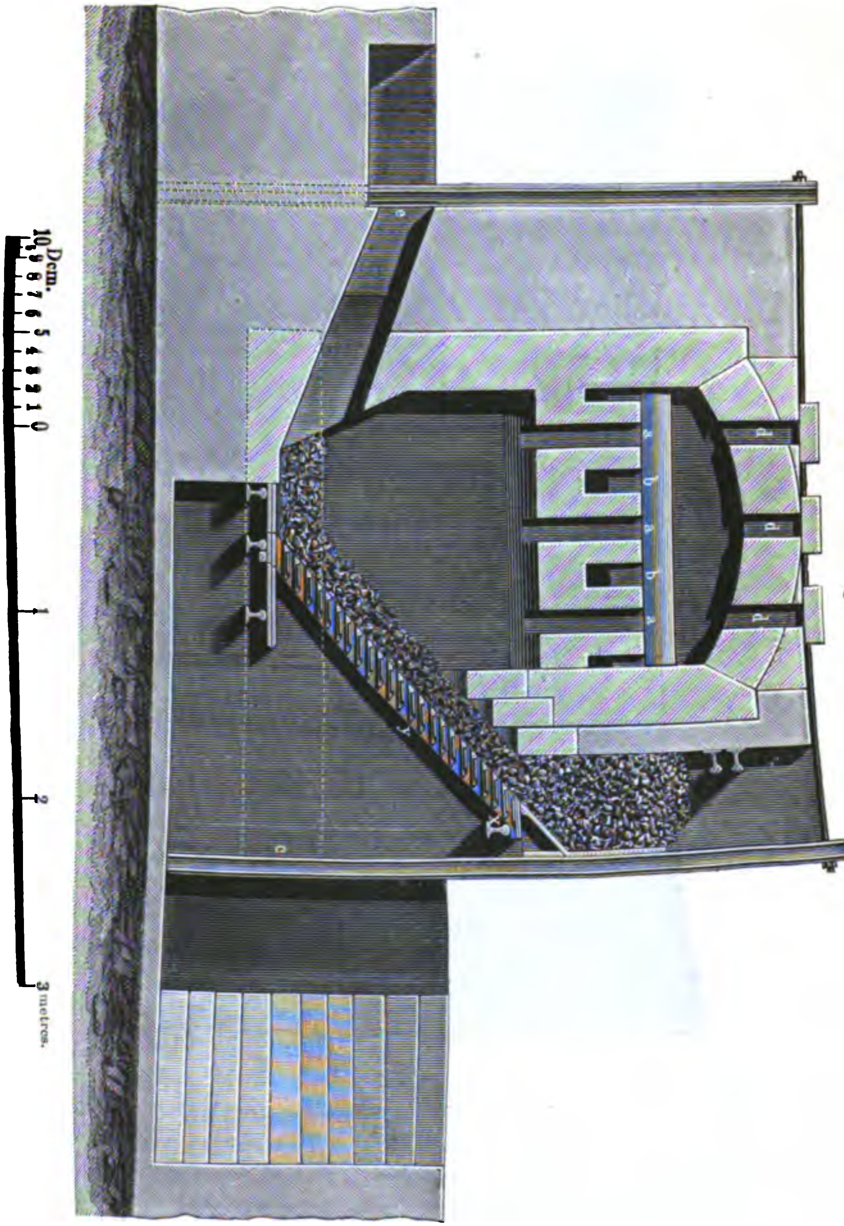
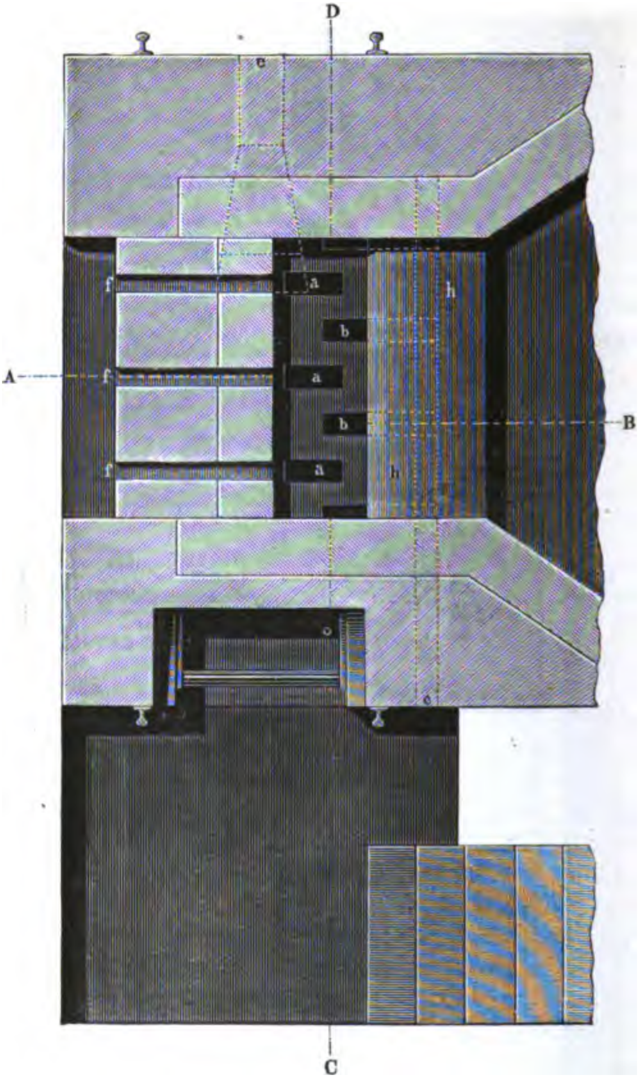


Fig. 231.

Fig. 232.



coals in the same time. Generally one carbonating-furnace is reckoned for each ball-furnace; but with forced work the former can do more than that. In the Lancashire finishing-furnaces, where no sawdust is used, twice the above amount of work can be done.

In "drying," a low heat must be employed, in no case up to visible red heat; the men mostly keep the door of *f* open to avoid overheating. The salt must be several times moved from the bridge towards the cooler portion of the bed. The interior of the furnace at this stage is quite invisible through the aqueous vapour arising. When no more steam is given off, the "carbonating" begins. This is the most difficult part of the work. The fire must now be increased, but only to a low red-heat, just a little above the melting-point of lead; by assiduous turning over of the mass the charred sawdust must be prevented from burning away without having acted upon all portions of the mass by the carbonic acid it gives out. The success of the operation thus entirely depends upon the skill of the furnaceman; it requires as much experience and care as balling, but less bodily exertion. On the Tyne this operation is also called "cleaning," because it is continued till the charred particles are all burnt, the caustic and sulphide are converted into carbonate, and the ash has assumed a clear appearance. This, of course, is all the easier the better the black salt, especially the freer it is from caustic and sulphide. Strongly caustic salt is very difficult and slow to carbonate, and gives great trouble by its liability to fluxing. Once the mass is fused, it cannot be cleaned any more, because the air has no access to its interior.

The last labour is that of "firing." The fire in the grate is touched up now, and the batch, with constant turning over and raking through with the tooth-rake, brought up to a bright red heat; this is done to completely burn the carbon and oxidize the sulphite and hyposulphite to sulphate. A somewhat caustic salt cannot get over this stage without softening; it "does not stand fire," and hence never gives such fine ash as salt nearly free from caustic. This is noticed more with the black salt from the front than with that from the back of the boiling-down pan. Unless the salt is ultimately exposed to a strong heat, the organic substances are not entirely destroyed, and on dissolving yield a coloured, badly settling liquor: this is worst when it has to be employed for making soda crystals. Only at this stage is the ferrocyanide destroyed; and the carbon separated thereby must be likewise burnt.

The tools of a carbonator on the Tyne are:—one paddle with wrought-iron head, 17×6 inches, $\frac{1}{2}$ inch thick, with a shank of 12 feet length and $1\frac{1}{4}$ inch thick; another paddle, with a head

2 feet × 4 inches, $\frac{5}{8}$ inch thick, bent up a little at the end, shank as before; a tooth-rake 12 inches broad, with 5 teeth of 4 inches × 1 inch, shank $\frac{3}{4}$ inch thick; a drawing-rake with wrought-iron head, 12 × 7 inches, shank 1 inch thick; a drawing-shovel, with a head 18 inches long × 12 inches broad, and an iron handle 8 feet long and $\frac{3}{4}$ inch thick; moreover the ordinary firing-tools and a poker 6 feet long and $1\frac{1}{4}$ inch thick.

The atmospheric oxygen has a considerable part to play in carbonating. In fact nearly or quite all the sodium sulphide of the tank-liquor is found in the ash, not as carbonate, but as sulphate. The assertion, made by Muspratt, that in this operation the sulphur is volatilized in some shape, is certainly correct only in a very restricted sense, if at all. For the above reason much more sulphate is found in soda ash than in black ash or even in tank-liquor. Even that sulphate which is locally reduced by the carbon of the sawdust, is reoxidized in the last firing. The sawdust and its charred remains have no doubt also the function of keeping the salt porous and accessible to the fire-gases and preventing fluxing, which occurs more easily before the caustic is removed.

A patent of Ward's (1846) proposes mixing the salt, before calcining, with 4 to 7 per cent. of magnesium carbonate, which in the furnace would give up its CO_2 to the NaOH and be converted into MgO; this on dissolving would remain behind and make the liquor settle better. Sawdust was to be used as well. This process has not been successful.

The temperature and the appearance of the batch generally sufficiently indicate the time for finishing the operation. But where the organic substances must be absolutely destroyed and a minimum of caustic left, which is especially important when the soda ash is to be employed for making crystals, it is best to make a direct testing, which the foreman can do in this way. He fills a tumbler a quarter full of soda ash (cooled on an iron shovel or the like), fills up the tumbler with tepid water, and at once stirs up well so as to prevent the mass caking together. He then allows the tumbler to stand a little while: if the liquor becomes perfectly clear and colourless, the ash is good; if the liquor is more or less of a yellow colour, so will also be the soda crystals made from it.

An investigation of the behaviour of black salt in the boiling-down pan with top heat and in the carbonating-furnace has been made by Moorhouse (Trans. Newcastle Chem. Soc. 1871, p. 17).

Unfortunately the portion referring to the furnace-work was not made with ordinary fair salt, but with very bad salt, containing much sulphide. From his observations on the changes of the liquor in the pans it is evident that the caustic in these was already partially carbonated, the liquor showing 12·9 to 22·2 caustic per cent. of carbonate, the salt only 11·6 to 17·6 per cent.; the average decrease of causticity in the pan was 4·7 per cent. of the whole available soda. [Moorhouse has not taken into account the accumulation of caustic in the red liquor, which must be charged with part of the above decrease]. The total sulphur, occurring as Na_2S, Na_2SO_4, and all intermediate stages of oxidation, increases but very slightly in the black salt as against the tank-liquor, about 0·04 to 0·12 per cent. of the soda; in the further treatment the total sulphur still increases a little, as the excess of sulphur in finished ash upon that in the tank-liquor is a little higher again. Perhaps this is only owing to the difficulty of taking samples; in any case it is a very small matter, viz. an increase of 0·10 to 0·21 per cent. sulphur from the liquor to the finished ash (excluding two cases, one much above and one much below the average, as not reliable). This difference represents the total contamination of the liquor in open pans by sulphate mechanically carried into it and by the sulphurous acid of the fire-gas; it is much less than is usually assumed.

More special observations were made with a black salt containing an abnormal quantity of caustic and sulphide, which yielded very bad ash, but still permitted the carbonating process to be followed in the furnace (see Table, p. 534). The furnace had been charged at 5.30 with a salt of the composition *a*; at 7, 8, and 9 o'clock the samples marked *b, c, d* were taken; and at 10.15 the ash marked *e* was drawn out, as it could not be carbonated any more. The analyses all refer to dry salt.

From this it follows that both the unoxidized sulphur and the caustic regularly decrease, but the former much more quickly than the latter; Na_2S soon diminishes to a trace, also the hyposulphite; the unoxidized sulphur is ultimately only present as sulphite, and only amounts to 2 per cent. of the total sulphur, 98 per cent. now being present as sulphate; in the beginning the proportion was 31 : 69. But, as we see, the caustic is much more difficult to treat, and up to the last cannot be got rid of entirely. It cannot be decided whether and to what extent the carbonating of the caustic in the furnace is due to the carbon of the sawdust or the car-

bonic acid of the fire-gases; but the 1·11 per cent. carbon initially present would suffice for the explanation of the action observed.

	a. Black salt.	*b.* 1¼ hour.	*c.* 2¼ hours.	*d.* 3¼ hours.	*e.* Soda ash.
Carbon (sawdust)	1·11	0·32	0·38	0·10	...
Insoluble	0·95	0·93	1·00	0·97	0·97
Na_2CO_3	78·30	79·04	80·05	81·07	81·86
NaOH	7·59	6·30	5·42	4·40	3·97
Na_2SO_4	7·71	9·12	10·27	10·85	11·06
Na_2SO_3	0·82	1·77	0·83	0·38	0·21
$Na_2S_2O_3$	1·05	trace	...	...	...
Na_2S	0·33	trace	trace	trace	trace
Percentage of unoxidized sulphur on total sulphur	31	17	8·3	3·6	2·0
Percentage of Na_2O present as NaOH, of the total Na_2O	11·4	9·5	8·2	6·9	6·0

It has been noticed that soda ash, even when drawn quite white out of the furnace, frequently turns yellow in the air after some time. It is certain that this is owing to the ferrous salt in the white ash being converted into ferric oxide. Frequently the total quantity of iron in an ash that turns yellow is not larger, but is even smaller, than in an ash that remains white; this alone seems to show that in the latter the ferrous oxide is protected from oxidation. Indeed, by titrating with permanganate the acidulated solution of a salt turning yellow (*a*), and of one not turning yellow (*b*), there were found :—

	per cent. Fe.	per cent. oxygen absorbed.
a.	0·020	0·0211
b.	0·018	0·0631

The action of the permanganate is owing to the presence of

sodium sulphite; and it is just this which prevents the oxidation of the iron and consequently the turning yellow of the ash.

If, therefore, the iron has not been previously removed, the turning yellow can still be avoided by purposely leaving a little sodium sulphide in the liquor, which forms sulphite. This holds good especially of caustic ash; for in carbonated ash the iron can be removed beforehand by well carbonating and completely settling. The iron arising from ferrocyanide has nothing to do with the question here.

After what we have said about the difficulty of carbonating with sawdust, it need excite no surprise that here also endeavours have been made to replace manual by *mechanical* labour. The conditions to be fulfilled are simple enough—drying at a moderate heat, then pulverizing and exposing to greater heat with frequent turning, so as to give the furnace-gases an opportunity of acting. But it was a long time before this goal was reached. In 1863, upon the suggestion of Messrs. Stevenson and Williamson, Napier constructed a very ingenious apparatus, which, however, turned out an engineer's job, not a chemical furnace, and, after costly trials, had to be abandoned again. It was a peculiar reverberátory furnace, with a bed consisting of a staircase sloping at an angle of 40 degrees, whose steps were constantly shaken singly by machinery. At the top it ended in a large hopper with a pair of feeding-rolls. In the hopper and on the steps the salt was dried, and on its way downwards was completely carbonated; at the bottom it was sifted and the coarser portions crushed by a roll. The whole was lifted by an elevator and passed through a second, similar furnace, in which the heat was much stronger, and where the proper calcining took place. Whilst the first part (drying the salt and impregnating it with caustic acid) was successfully performed, the second furnace was constantly stopped up by fluxings and turned out unmanageable.

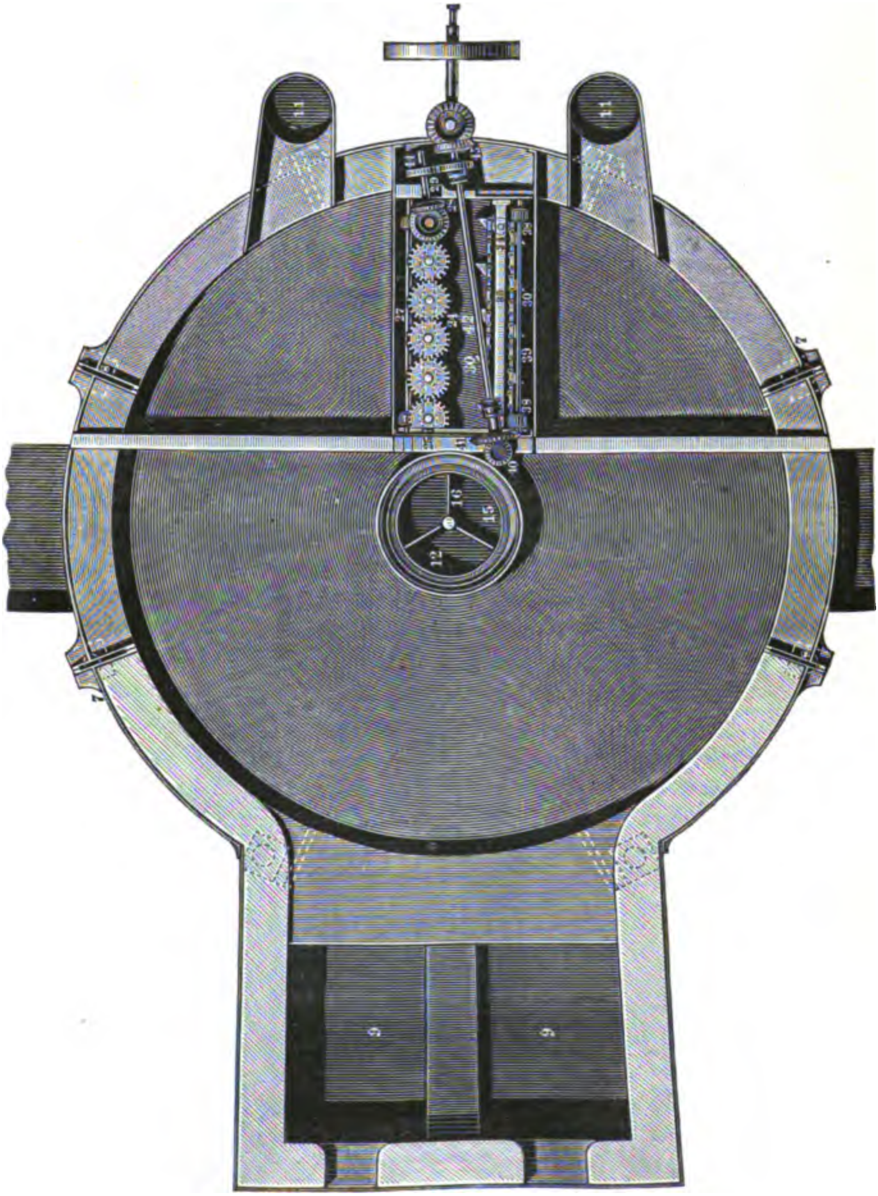
The object has recently been completely attained by employing furnaces with a circular revolving hearth, which have been used for metallurgical purposes for a long time past (comp. for instance Gibb and Gelstharpe's copper-calcining furnace, Vol. I. p. 598). This seems to have been done first by Churchill; then followed a construction by Schofield (patented in 1875, No. 511), which contains nearly all the features of the furnaces actually in use. These have been constructed by Mactear (patent of May 17th, 1876), whose only inno-

vation upon Schofield's furnace was that of discharging the furnace in the centre instead of at the periphery. But over and above this he has the considerable merit of having, by very substantial construction, made of the furnace a working concern, which fulfils all demands and which is more and more generally introduced into the large factories. Mactear's furnace is shown in figs. 233 and 234, in plan and sectional elevation.

The circular furnace-bottom, 1, 20 feet in diameter, consists of boiler-plate lined with fire-brick, and is fixed on frame-pieces, 2, which are fitted with wheels, 3, arranged to run on a circular flanged tram-plate, 4, fixed beneath the furnace. The furnace-bottom, 1, is made with a raised rim, 5, and is covered by a roof or arch, 6, of fire-brick carried by arc-shaped girders, 7, which are supported on pillars, 8, indicated by dotted lines in fig. 233. The arch, on 20 feet span, has only 18 inches rise, and is quite stable although it looks quite flat from the top. For these arches as well as for the whole furnaces the excellent bricks of the Glenboeg Fire Brick Company are recommended. Two fireplaces, 9, communicate by a passage, 10, with the interior of the furnace; and the fire passes off by two exit-flues, 11, nearly opposite to the inlet-passage, 10. For charging the furnace, one or more openings (not shown in the drawings) which are closed when the furnace is in operation, are provided at any convenient part of the roof, 6.

The discharging takes place by a nearly cylindrical opening, 12, made quite through the bottom 1 and its lining at the centre; and this opening is fitted with an iron casing, 13, of 3 feet 6 inches diameter, which projects below the bottom. A somewhat larger opening, 14, is formed through the roof, 6, and is fitted with an iron lining (4 feet in diameter). The discharge-opening is closed by an iron cylinder, 15, jacketed with fire-brick, which, when in the closing position, as shown in fig. 234, rests on the top edge of the iron lining, whilst its upper part closes the opening in the roof 6. The closing-valve 15 is made with two sets of arms, 16, 17, to the upper set of which there is attached an eye-bolt for the connexion of a chain, 18, for raising the valve, whilst to the lower set, 17, there is attached a spindle, 19, which passes through a guide, 20, fixed by arms in the opening 12 below. Air is allowed to pass up through the discharge-opening 12 and the valve 15, so as to prevent the metal parts from becoming overheated. The discharge-

Fig. 233.



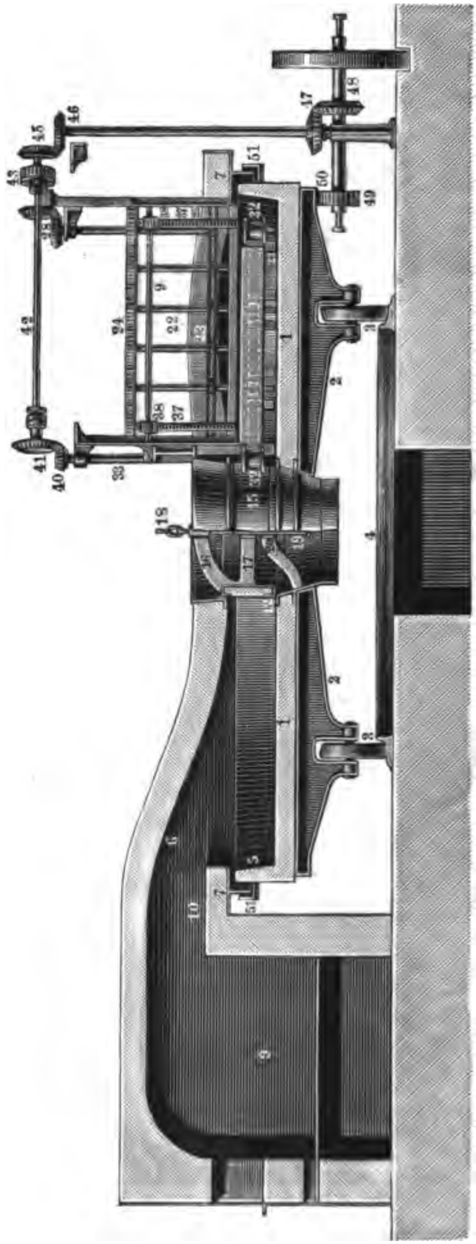


Fig. 234.

hole 12 is opened to the interior of the furnace by raising the cylindrical valve 15 into the recess 14 in the roof 6; and the contents of the furnace may then be discharged into a waggon placed beneath the furnace.

During the work the circular furnace-bottom revolves slowly, and the mass in it is constantly turned over by a stirring-apparatus (in the same way as already indicated by Schofield). It acts between the central valve 15 and the outer rim 5, at the part between the two exit-flues 11; so that the fire does not touch it; and it comprises a set of forks, 21, fixed on the lower ends of vertical shafts, 22, which are held in a frame, 23, and geared together by spur-wheels, 24, at their upper ends, so as to rotate in alternate directions; the forks 21 are disposed diametrically, being arranged so as not to interfere with each other, although they are large enough to work over overlapping areas. The stirring-apparatus can be raised out of action or lowered more or less as may be required, the frame 23 being fitted to slide in vertical guides, 25, on a fixed framing, and being formed with vertical racks, 26, with which there gear pinions on a horizontal shaft, 27, arranged to be turned by means of a crank-handle. The driving-power is applied to the outermost of the vertical stirrer-shafts 22, which is elongated to pass up through a bevel wheel, 28, to which it is geared by a groove and feather permitting its vertical movement with the frame 23. The bevel wheel 28 gears with a bevel wheel on a short horizontal shaft, 29, driven as described.

The finished charges of materials may be pushed towards the central discharge-opening 12 by manual labour; but it actually is done mechanically by means of a series of pushers or scrapers, 30, attached to an endless chain, 31, carried and moved by pulleys, 32, on the lower ends of movable shafts, 33, 34. The latter are carried by a frame, 35, which is fitted to work in vertical guides, 36, and has racks, 37, on it in gear with pinions, 38, on a horizontal shaft, 39, so that it can be raised or lowered, as required, by means of a crank-handle. The discharging-apparatus is worked by means of one (33) of the vertical shafts, which is elongated to pass up through a bevel wheel, 40, connected to it by a groove and feather, to permit the vertical movement of the frame 35. The bevel wheel 40 is in gear with a bevel wheel, 41, on a horizontal shaft, 42, which has also on it a spur-wheel, 43, gearing with a spur-wheel, 44, on the horizontal shaft 29 of the stirring-apparatus.

The shaft 29 has on it clutches in connexion with the wheels 41 and 43, so that either can be put into or out of gear as required; and this shaft (42) is itself driven, by means of the bevel wheels 45, by a vertical shaft, 46, geared by bevel wheels, 47, to the shaft 48, which imparts rotation to the furnace-bottom 1, and is driven, by means of a pulley and belt, or otherwise, by a suitable prime mover. The furnace-bottom is turned by a pinion, 49, on the shaft 48, and gearing with a circular rack, 50, fixed to the framing of the furnace-bottom. A gutter, 51, is formed round the outside of the rim 5 of the furnace-bottom, to contain loose soda-ash or sand, into which the vertical flanges of the girders 7 dip, so as to form a close connexion between the rotating furnace-bottom 1 and fixed roof 6, as usual in furnaces with rotating bottoms.

A considerable number of such furnaces (30 in 1878) already exist, both on the Tyne, at Glasgow, in Lancashire, and in France; and more of them are constantly being built, in spite of a very high patent-royalty. They usually turn out 3½ tons of ash in six or seven hours. The filling and discharging take some additional hours; so that, on the whole, in six days about 110 tons can be turned out, if the usual 2 per cent. of caustic is left in the ash, but only 90 tons if the carbonating is to be driven to the utmost. It is possible to get down to 0·25 per cent. caustic even with saw-dust, without carbonating by gas, if special care be taken; hence ultimately a much higher heat can be applied and white ash made. This product is excellently adapted for soda crystals, especially as the ferric oxide in it is in a very dense state and readily settles on dissolving; it is also denser than that made by hand, so that one tenth of the number of casks are saved. The consumption of coals, according to reliable information, is no less than with hand furnaces, viz. 40 per cent. of the weight of ash, without reckoning the steam. The principal saving is in labour, the latter costing 1*s*. to 1*s*. 6*d*. per ton against 3*s*. 6*d*. to 4*s*. with hand furnaces. A single mechanical carbonator replaces on the Tyne six hand furnaces—in Lancashire (where no saw-dust is used) not quite so many.

The following Table, published by Mactear (Journ. Soc. Arts, 1878, p. 561), shows the progress of the reaction in an operation; all the figures signify per cent. of available soda.

No.	Time.	NaOH.	NaCl.	$Na_2S_2O_3$.	Na_2SO_3.	Na_2SO_4.	All calculated as Na_2SO_4.	Na_2S.	Remarks.
1.	h m 3 0	15·17	3·26	2·87	2·12	3·88	13·33	1·0406	Wet salt.
2.	3 30	13·25	3·29	4·69	0·53	3·81	13·33	0·2582 0·10757	Charging completed, still wet.
3.	4 0	11·20	3·18	4·60	1·00	3·80	13·48	0·0965	Damp.
4.	4 30	5·40	3·28	0·86	3·75	7·31	13·43	0·06308	Dry.
5.	5 0	2·87	3·28	0·72	1·44	10·37	13·38	0·0313	Quite dry.
6.	5 30	1·90	3·28	0·59	0·23	12·03	13·42	0·0126	Nearly red hot.
7.	6 0	1·75	3·29	0·19	0·04	12·93	13·48	trace.	Red hot.
8.	6 30	1·61	3·28	nil.	0·04	13·39	13·48	nil.	"
9.	7 0	1·46	3·28	"	0·04	13·40	13·49	"	"
10.	7 30	1·31	3·28	"	0·04	13·45	13·45	"	"
11.	8 0	1.31	3·28	"	0·04	13·45	13·45	"	"

The question whether there is not slightly more mechanical loss of soda in Mactear's furnace than in the ordinary carbonating furnaces, owing to the continuous stirring in a strong draught, is not yet finally decided. The extremely finely divided state of the soda ash in Mactear's furnace would seem to favour this; but in the worst case it can only be a very slight loss.

CHAPTER IX.

COMMERCIAL SODA ASH.

Good calcined soda ash, such as is obtained according to our description, should be, whether hot or cold, of a white colour, not yellow or reddish; but it cannot be expected to be as white as "refined alkali." Frequently a yellowish ash is better carbonated than a purely white one; this will be the case if iron salts are present in large quantity, which by stronger calcining form ferric oxide and then stain the ash. Often the colour is bluish, either from ultramarine or from sodium manganate. When it is grey, this is a sign of bad carbonating and calcining; it then contains much caustic and sulphide. Good ash after grinding should show but few black or red specks.

Its *caustic*, except in the case of "caustic ash," should never exceed 2 per cent. when it is intended for making soda crystals; the maximum of NaOH is sometimes fixed at 1 per cent., which is not easy to manage if all the liquors are worked into the ash and the carbonating has been effected by sawdust, not by gas. Mactear's mechanical carbonator alone makes it easy. *Sulphide* ought not to be traceable by lead paper even in a moderately carbonated ash; a solution of 1 gram, to which a solution of starch has been added, should be turned blue by the first drop of iodine solution. An alkaline solution of lead (sodium plumbate) acts better than lead paper. Still a soda ash, made as described, is never exempt from small traces of lower degrees of oxidation; these, however, can only be found if large quantities, say 50 grams, are analyzed. An ordinary soda ash must be taken as up to the commercial standard, if it contains not more than 0·1 per cent. of oxidizable sulphur compounds; mostly even two or three times as much do no harm. The most

delicate analytical method for minute quantities of sodium sulphide is that of Lestelle (p. 447). Hyposulphite cannot occur in calcined ash, as it is already destroyed at a commencing red heat. Sulphite occurs almost regularly, but in small quantity, in ordinary commercial soda ash; it can be detected by iodine solution and other well-known reagents.

Of *insoluble substances* good soda ash should not contain more than 1 or 1¼ per cent.; 1½ per cent. must be considered the maximum. It consists principally of calcium carbonate with a little alumina and silica and minimal quantities of iron, but more of this in very yellow descriptions of ash. The *moisture* in fresh ash should not exceed ¼ to ½ per cent., and even after some time not much above 1 per cent. With 2 per cent. moisture the ash is often already lumpy and discoloured.

Two salts regularly found in soda ash, viz. sodium chloride and sulphate, are hardly ever injurious; but neither are they useful, at any rate in the quantities contained in ordinary soda ash. They are accordingly not estimated in daily practice, but only for special purposes. Still the manufacturers ought at least once a week to make a detailed analysis of an average sample of the ash produced, in order to follow up the process: this ought to comprise total alkalinity, caustic, oxidizable sulphur, chloride, sulphate, insoluble substances, and moisture. A number of complete analyses of soda ash will be given in a table later on. For daily control it suffices to test the work of every carbonator for total available soda and caustic, and, in the case of very caustic ash, also for its behaviour towards iodine solution.

It need not be mentioned that, in *sampling*, great care must be taken to obtain a really average sample; this is not very easy to do with unground ash, which, indeed, for this reason can hardly be guaranteed down to one quarter per cent., because the lumps and the powder differ in strength. Only by taking very large samples can the proportion between lumps and powder be approximately hit. For sampling ground ash in casks a peculiar iron or steel tool is employed (fig. 235), which must be kept free from rust and quite bright. It is introduced into the cask through a 1¼-inch hole bored in one of its ends, as far as possible, with a screwing motion, so that its hollow space becomes filled with the different layers of ash in the cask, and then quickly pulled out.

It is always advisable to dissolve a much larger quantity of soda

ash than is required for one test: thus with a quick and rough weighing as much accuracy is attained as by weighing a small sample on a fine balance; the larger quantity of the sample will also more nearly represent the average quality; and several tests can be

Fig. 235.

made very quickly in this way. For quick work the following plan can be recommended. Twice the equivalent of Na_2O in decigrams, *i. e.* 6·2 grams, is dissolved in a 200 or 250 flask, filled up to the mark; after settling, one tenth of the liquor is taken out with a pipette (filtering is unnecessary in this case, as the pipette can be used without at all disturbing the insoluble residue) and titrated with standard acid. Since the quantity titrated, viz. 0·62 gram, if it were pure Na_2O, would require 20 cub. centims. of a normal acid (saturating 0·031 of Na_2O per cub. centim.), each $\frac{20}{100} = 0{\cdot}2$ cub. centim. of acid indicates 1 per cent. Na_2O. If more accurate work is required, twice the quantity is taken for testing, so that each 1 per cent. corresponds to 0·4 cub. centim. of normal acid, &c.

The caustic is estimated in another portion of the same solution, by precipitating it with barium chloride, diluting to a certain volume, filtering off one half, and titrating the filtrate. Siegwart (Wagner's Jahresb. 1874, p. 305) for this purpose weighs off 5 grams, dissolves it in 100 cub. centims. of tepid water, and hangs upon the side of a beaker a strip of well-made turmeric paper, which is coloured crimson by sodium carbonate, but vermilion by caustic soda. If now dilute sulphuric acid be added drop by drop, it will first saturate the caustic; and at the moment when this is done the paper turns crimson. It is also prescribed to estimate the caustic by first titrating the ash in the usual way, and then estimating the loss of weight in a Fresenius-Will carbonic-acid apparatus; the dif-

ference is taken as NaOH. This plan is both more tedious than that with barium chloride and less reliable, since the sulphite is calculated as NaOH. In either case this will be done with Na_2S; but its quantity in ordinary soda ash is too minute to sensibly influence the estimation of caustic.

At some works they do not titrate a filtered or settled solution, but the muddy one obtained at first. Since the insoluble is mostly calcium carbonate, the alkalimetrical test will thus come out too high; hence this plan is objectionable. But it is not a sensible loss to the buyer that, universally, not merely the sodium carbonate but all other soluble salts affecting the test acid, viz. sodium hydrate, aluminate, and silicate, are estimated by the usual degrees; all these in nearly all cases are quite analogous to sodium carbonate in their action, except in the manufacture of crystal soda. The sulphite cannot, and still less can the sulphide, sensibly affect the alkalimetrical test. This itself has been fully described in a previous chapter (Vol. I. p. 44 *seqq.*), to which we must refer the reader. The process just mentioned, of Fresenius and Will, is probably very little employed in alkali-works for testing soda ash, which for that purpose must first be treated with ammonium carbonate to carbonate the caustic. It is more adapted for occasional testing by those not possessing standard acid or volumetrical apparatus.

The *commercially used degrees* of soda ash are different with each of the three principal industrial nations. In England they mean the percentage of "real" or "available" soda (Na_2O); in Germany, the percentage of sodium carbonate; in France, the degrees of Descroizilles's arbitrarily fixed test. The German degrees for ordinary soda ash would appear to be the most rational, since that ash essentially consists of sodium carbonate; but it is chargeable with the inconsistency of quoting as carbonate all other sodium salts which act upon the test acid. This does not matter very much for soda ash; but it looks absurd when applied (as usual in Germany) to caustic soda as well, where the strength is stated in a percentage of a substance occurring only as an impurity, and where upwards of 120 per cent. regularly comes out. More rational is the English way of quoting the percentage of "available" soda (Na_2O)—that is to say, all soda salts acting on the test acid which, *e. g.* in soapmaking, act just like carbonate. These degrees in France are called "Gay-Lussac's degrees," but are never employed in practice. Pure sodium carbonate would show 58·49 English

degrees; but since, according to the old notation, the soda (Na_2O) is also understood as being contained in the hydrate, the same degrees are quite correctly employed for caustic as well. If in England a soda ash is called "52 per cent.," this only means that the test acid neutralized by it corresponds to $\frac{52}{100}$ of the Na_2O employed; but the latter may be represented by carbonate, silicate, aluminate, hydrate, nay, even by sulphide. It is often distinctly added that, say, 2 per cent. of the whole is present as caustic ($NaOH$). On the other hand the name "70-per-cent. caustic soda" means that it corresponds to $\frac{70}{100}$ Na_2O, equal to 90·3 per cent. $NaOH$—supposing that no sodium carbonate is present, which, however, always does occur.

Unfortunately this very rational English system of signifying the strength of alkali has been damaged by an error which, so far, has been only to a small extent eliminated. Most factories assume the equivalent of soda to be not $=31$, as it really is, but $=32$, and standardize their acid accordingly. Whether originally this error was accidental or wilful, cannot now be made out. It causes the ordinary commercial degrees to mean a *less* percentage of real Na_2O, or, in other words, to make the ash appear stronger than it is. In this there is a difference between the Tyne test and the Liverpool test. On the Tyne the equivalent of sodium carbonate is taken as 54 instead of 53, and the test acid made so that a litre of it saturates 54 grams pure Na_2CO_3. Chemically pure Na_2CO_3 consequently with this acid will show $\frac{32}{54}=59{\cdot}26$ per cent., instead of 58·49 per cent. of "real" soda (that is, 0·77 per cent. too much); each Tyne degree therefore indicates 1·316 per cent. of its amount *more* than the real soda; *e. g.* 50 real Na_2O shows $50+50\times0{\cdot}0136$ $=50{\cdot}66$ Tyne degrees. The same degrees are also adopted by all other respectable analytical chemists in Great Britain, with the sole exception of Liverpool, where a way of stating the results of testing ash has obtained, not at all explicable by a mere error, but only by the desire of deceiving the buyer. They reason thus:—"Because the 'old' equivalent of pure sodium carbonate is $\frac{1}{54}$ larger than the 'new,' we need only increase our percentages, found by the real equivalent, by $\frac{1}{54}$, in order to obtain commercial degrees; *e. g.* we call real 53-per-cent. Na_2O, 54-per-cent." There is a fallacy at the bottom of this; for the Na_2O in the Na_2CO_3 must equally increase its equivalent: according to Tyne degrees, which take account of this, 53 Na_2O are only 53·70 degrees. Nay, some

Lancashire "chemists" go beyond this, and reason, "Since the 'old' equivalent of soda is $\frac{1}{31}$ larger than the 'new,' we add to each real per cent. Na_2O another $\frac{1}{31}$ to get at commercial degrees." In this case, *e. g.*, 50 per cent. Na_2O will become $50+50\times\frac{1}{31}=51{\cdot}6$ degrees! Even this does not satisfy some; one Liverpool firm of analytical chemists especially, very popular of course with the alkali-manufacturers of that district, sometimes states the strength of soda ash 2 or 3 per cent. above the real strength, and carries this on unblushingly, although this scandal has been publicly exposed several times, and that very energetically (comp. Chem. News, xxxii. pp. 267, 280, 302; xxxiii. pp. 8, 17, 31, 40). It has been shown that a good profit can be made by buying according to Newcastle test and selling, nominally at the same price, according to Liverpool test. Some of the largest English firms (Tennant's, Jarrow, Allhusen, and others) now sell by *real* percentage of Na_2O; but even the large Liverpool firms refuse to do this.

Decidedly the most irrational of all degrees are those of Descroizilles, universally employed in France. They show how many parts by weight of sulphuric hydrate, SO_4H_2, are saturated by 100 parts of the substance employed—that is, a totally arbitrary unit. Since the equivalents of Na_2CO_3 and SO_4H_2 are in the ratio of 53 : 49, 100 pure sodium carbonate require 92·45 SO_4H_2, or show as many degrees Descroizilles. The only thing which can be said for this way of stating the strength is that, without any inconsistency, it can be employed for caustic soda; this advantage, however, is shared by the real English degrees, which are called Gay-Lussac degrees by the French. Descroizilles degrees are also applicable to potash, and at a glance represent the alkalimetrical equivalents of soda and potash; but this is a point not frequently important in practice.

In order to save the troublesome reduction of one kind of degree to another, Pattinson (Chem. News, xix. p. 112) has calculated a comparative table for per cents. of real Na_2O, of Na_2CO_3 (German degrees), of Tyneside or Newcastle degrees, and of Descroizilles degrees. It only begins at 30 per cent. Na_2O; but as lower degrees (*e. g.* of causticity) have often to be compared as well, we have extended the table down to 1 per cent. Na_2O.

TABLE.

Gay-Lussac's degrees. Na_2O.	German degrees. Na_2CO_3.	Newcastle degrees. Na_2O.	Descroiz. degrees. SO_4H_2.	Gay-Lussac's degrees. Na_2O.	German degrees. Na_2CO_3.	Newcastle degrees. Na_2O.	Descroiz. degrees. SO_4H_2.
0·5	0·85	0·51	0·79	26·5	45·31	26·85	41·88
1	1·81	1·01	1·58	27	46·17	27·35	42·67
1·5	2·56	1·52	2·37	27·5	47·02	27·86	43·46
2	3·42	2·03	3·16	28	47·88	28·36	44·25
2·5	4·27	2·54	3·95	28·5	48·73	28·37	45·04
3	5·13	3 04	4·74	29	49·59	29·38	45·83
3·5	5·98	3·55	5·53	29·5	50·44	29·89	46·62
4	6·84	4·05	6·32	30	51·29	30·39	47·42
4·5	7·69	4·56	7·11	30·5	52·14	30·90	48·21
5	8·55	5 06	7 90	31	53·00	31·41	49·00
5·5	9·40	5·57	8 69	31·5	53·85	31·91	49·79
6	10·26	6 08	9·48	32	54·71	32·42	50·88
6·5	11·11	6·59	10·27	32·5	55·56	32·92	51·37
7	11·97	7·09	11·06	33	56 42	33·43	52·16
7·5	12·82	7·60	11·85	33·5	57·27	33·94	52·95
8	13·68	8·10	12·64	34	58·13	34·44	53·74
8·5	14·53	8·61	13·43	34·5	58·98	34·95	54·53
9	15·39	9·12	14·22	35	59·84	35·46	55·32
9·5	16·24	9·63	15·01	35·5	60·69	35·96	56·11
10	17·10	10·13	15·81	36	61·55	36·47	56·90
10·5	17·95	10·64	16·60	36·5	62·40	36·98	57·69
11	18·81	11·14	17·39	37	63·26	37·48	58·48
11·5	19·66	11·65	18·18	37·5	64·11	37·98	59·27
12	20·52	12·17	18·97	38	64·97	38·50	60·06
12·5	21·37	12·68	19·76	38·5	65·82	39·00	60·85
13	22·23	13·17	20·55	39	66·68	39·51	61·64
13·5	23·08	13·68	21·34	39·5	67·53	40·02	62·43
14	23·94	14·18	22·13	40	68·39	40·52	63·22
14·5	24·79	14·69	22·92	40·5	69·24	41·03	64 01
15	25·65	15·19	23·71	41	70·10	41·54	64·81
15·5	26·50	15·70	24·50	41·5	70·95	42·04	65·60
16	27·36	16·21	25·29	42	71·81	42·55	66·39
16·5	28·21	16·73	26·08	42·5	72·66	43·06	67·18
17	29·07	17·22	26·87	43	73·52	43·57	67·97
17·5	29·92	17·73	27·66	43·5	74·37	44·07	68·76
18	30·78	18·23	28·45	44	75·23	44·58	69·55
18·5	31·63	18·74	29·24	44·5	76·08	45·08	70·34
19	32·49	19·25	30 03	45	76·94	45·59	71·13
19·5	33·34	19·76	30·82	45·5	77·80	46·10	71·92
20	34·20	20·26	31·61	46	78·66	46·60	72·71
20·5	35·05	20·77	32·40	46·5	79·51	47·11	73·50
21	35·91	21·27	33·19	47	80·37	47·62	74·29
21·5	36·76	21·78	33·98	47·5	81·22	48·12	75·08
22	37·62	22·29	34·77	48	82·07	48·63	75·87
22·5	38·47	22·80	35·56	48·5	82·93	49·14	76·66
23	39·33	23·30	36·35	49	84·78	49·64	77·45
23·5	40·18	23·81	37·14	49·5	84·64	50·15	78·24
24	41·04	24·31	37·93	50	85·48	50·66	79·03
24·5	41·89	24·82	38·72	50·5	86·34	51·16	79·82
25	42·75	25·32	39·51	51	87·19	51·67	80·61
25·5	43·60	25·83	40·30	51·5	88·05	52·18	81·40
26	44·46	26·34	41 09	52	88·90	52·68	82·19

TABLE (continued).

Gay-Lussac's degrees. Na_2O.	German degrees. Na_2CO_3.	Newcastle degrees. Na_2O.	Descroiz. degrees. SO_4H_2.	Gay-Lussac's degrees. Na_2O.	German degrees. Na_2CO_3.	Newcastle degrees. Na_2O.	Descroiz. degrees. SO_4H_2.
52·5	89·76	53·19	82·98	65·5	111·99	66·36	103·53
53	90·61	53·70	83·77	66	112·85	66·87	104·32
53·5	91·47	54·20	84·56	66·5	113·70	67·37	105·11
54	92·32	54·71	85·35	67	114·56	67·88	105·90
54·5	93·18	55·22	86·14	67·5	115·41	68·39	106·69
55	94·03	55·72	86·93	68	116·27	68·89	107·48
55·5	94·89	56·23	87·72	68·5	117·12	69·40	108·27
56	95·74	56·74	88·52	69	117·98	69·91	109·06
56·5	96·60	57·24	89·31	69·5	118·83	70·41	109·85
57	97·45	57·75	90·10	70	119·69	70·92	110·64
57·5	98·31	58·26	90·89	70·5	120·53	71·43	111·43
58	99·16	58·76	91·68	71	121·39	71·93	112·23
58·5	100·02	59·27	92·47	71·5	122·24	72·44	113·02
59	100·87	59·77	93·26	72	123·10	72·95	113·81
59·5	101·73	60·28	94·05	72·5	123·95	73·45	114·60
60	102·58	60·79	94·84	73	124·81	73·96	115·39
60·5	103·44	61·30	95·63	73·5	125·66	74·47	116·18
61	104·30	61·80	96·42	74	126·52	74·97	116·97
61·5	105·15	62·31	97·21	74·5	127·37	75·48	117·76
62	106·01	62·82	98·00	75	128·23	75·99	118·55
62·5	106·86	63·32	98·79	75·5	129·08	76·49	119·34
63	107·72	63·83	99·58	76	129·94	77·00	120·13
63·5	108·57	64·33	100·37	76·5	130·79	77·51	120·92
64	109·43	64·84	101·16	77	131·65	78·01	121·71
64·5	110·28	65·35	101·95	77·5	132·50	78·52	122·50
65	111·14	65·85	102·74				

Will and Fresenius proposed to designate alkali according to its content of moisture. The value of the alkali was to be indicated by a fraction the numerator of which was to express the alkalimetrical degree, and the denominator the percentage of moisture. $\frac{84}{108}$ means that the *dry* alkali corresponds to 84 per cent. Na_2CO_3, but that it contains so much water that 100 parts dry soda would be contained in 108 parts of it. This style has not met with general acceptance; it is not called for, since alkali with more than 2 per cent. of moisture is too much discoloured and lumpy to be a saleable product.

The Composition of Soda Ash.

Many analyses of soda ash have been made; but most of them have but a limited interest, since the composition of alkali varies very much even at the same works. We shall in the first place quote some published analyses.

	French samples of carbonated and refined alkali (Tissandier, Monit. scient. 1868, p. 979).					French samples of caustic ash (sels caustiques) (Tissandier).				Ring-Kuhl (Unger).	Liverpool.		Refined alkali.	Glasgow soda ash (Bolley).
											Soda ash for soap (Muspratt and Danson).	White alkali for plate glass. (Muspratt and Danson).		
Sodium carbonate...	76·67	87·01	92·34	95·39	98·20	82·47	88·09	84·54	81·67	62·13	77·08	78·55	98·20	80·64
,, hydrate ...	...	...	...	...	...	2·11	6·25	7·12	10·25	17·20	4·88	4·15	...	...
,, sulphide ...	...	...	...	...	...	...	...	...	...	...	0·63 ?	...	...	0·55 ?
,, sulphite ...	...	...	...	...	...	...	...	...	...	0·35	...	...	...	...
,, sulphate ...	8·51	3·25	2·15	1·50	0·35	8·80	1·62	2·15	2·50	8·66	5·11	1·70	0·35	0·65
,, chloride ...	12·48	6·41	3·28	2·11	0·99	4·32	2·43	3·50	4·11	3·41	7·13	5·62	0·99	7·66
,, silicate......	...	...	...	...	...	...	...	...	...	2·56	2·40	0·25	...	...
,, aluminate..	...	...	...	...	...	...	...	...	...	1·11	...	...	...	...
Calcium carbonate...	...	...	...	...	...	...	...	...	...	...	0·32	0·33	...	0·07
Ferric oxide	...	...	...	...	...	...	...	...	...	...	0·32	0·27 ?	...	...
Insoluble	0·12	0·22	0·08	...	0·06	0·12	0·11	0·21	0·09	0·62	0·66	0·48	0·06	1·29
Moisture	2·22	3·11	1·15	1·00	0·40	2·10	1·50	2·48	1·38	3·96	1·06	8·65	0·40	8·43

	Black salt uncalcined.		Caustic ash from the same.		Black salt for carbonated soda.		Carbonated soda ash.		Alkali refined by dissolving and calcining.		Calcined soda crystals.		Soda crystals.	
	I.	II.	I.	II.	I.	II.	I.	II.	I.	II.	I.	II.	I.	II.
Sodium carbonate...	68·907	65·513	71·614	70·461	79·641	80·918	84·002	83·761	84·314	84·721	98·120	97·984	36·47	36·93
,, hydrate ...	14·433	16·072	11·231	13·132	2·712	3·924	1·060	0·734	trace	0·280	...	...	...	...
,, sulphate ...	7·018	7·812	10·202	9·149	8·641	7·431	8·560	9·495	10·260	9·764	1·076	1·124	0·94	0·54
,, sulphite ...	2·231	2·134	1·117	1·136	1·238	1·110	trace	0·386	trace	...	...	...	...	...
,, hyposulphite...	trace	trace	...	...	trace	trace	...	...	...	...	...	...	...	...
,, sulphide ...	1·314	1·542	...	...	trace	0·230	...	...	...	...	...	...	...	...
,, chloride ...	3·972	3·862	3·051	4·279	4·128	3·142	3·222	3·287	3·480	3·140	0·742	0·563	0·42	0·31
,, aluminate..	1·016	1·232	0·923	0·734	1·176	1·014	1·013	0·620	0·632	0·716	...	...	...	...
,, silicate......	1·030	0·800	1·042	0·986	1·234	1·317	0·984	0·780	0·414	0·318	...	...	...	...
Insoluble	0·814	0·974	0·316	0·464	0·972	0·768	0·716	0·846	0·250	0·498	...	...	Water: 62·15	62·21
Total............	100·735	99·941	99·496	100·341	99·742	99·854	99·557	99·909	99·350	99·437	99·938	99·671	99·98	99·99

The progress made by alkali as it passed through the different purifying operations is clearly shown in Brown's table, p. 552 (Phil. Mag. [3] xxxiv. p. 15); but it must be said that nowadays they would not reflect much credit upon the factory where the alkali was made.

Some of the above analyses must be received with great caution. For instance, 0·63 and 0·55 sodium sulphide seem incredibly high quantities to be found in soda ash. In a sample of alkali, cited as "refined" and specially intended for plateglass-making, 0·27 per cent. Fe_2O_3 is said to have occurred, which is again incredible. In the French analyses the silicate and aluminate are evidently comprised in the carbonate. The quantity of moisture in some of the samples proves that they were very old. Altogether the quoted analyses of soda ash are not characteristic of the present state of the alkali-manufacture.

Grinding and Packing Soda Ash.

Most of the soda ash sent into the trade is first *ground.* In this state it looks much better than unground; it is more easily handled by the consumer; and the cost of grinding is less than the extra cost of casks for unground ash, which occupies 50 per cent. more space. Caustic ash only is usually sold unground: it is very difficult to grind, probably owing to its attraction for moisture; for even ordinary soda ash is much more difficult to grind when it has become quite cold and attracted ever so little moisture.

For grinding soda ash, either edge-runners with cast-iron pan and cast-iron rollers, or horizontal mills, just like corn-mills, are employed. The former yield a very fine product, but require more power for the same output than horizontal mills, and involve sifting the ground-stuff, which is unnecessary with the latter. Hence edge-runners are rarely used now, except for crushing the large and hard lumps which very much injure the mill-stones.

The horizontal mills need not be described here, as they are quite similar to ordinary flour-mills; but it should be mentioned that "French burrs" are not suitable, and that blue lava stones are preferred (*e.g.* those from Andernach on the Rhine), which are not so hard as the French burrs, and stand the hot soda much better without cracking.

In a few places Carr's disintegrators, or some of the more

modern crushing-apparatus, may be employed for grinding soda ash.

The ground alkali always falls direct into *casks*, which stand on a movable truck running on a tramway; so that when one cask is full it is easily moved on, and a new cask on its truck can be pushed into its place. The way of filling the casks is of great importance. The usual size of soda-ash casks on the Tyne and the Clyde is 3 ft. 4 in. high and 2 ft. 8 in. wide. Such a cask, loosely filled with ash as it falls in from the mill, holds only 6 to 7 cwt. If shaken up from time to time and knocked with a mallet, it holds 11 or 12 cwt., sometimes more; and this should be asked for as a minimum. But it takes less labour and injures the casks less if a simple eccentric is attached to the mill, which gently and constantly shakes the truck upon which the cask rests; the latter then holds as much as 15 cwt. The casks for such weights must be made strong, not merely of soft wood, but partly of larch or oak staves. In Lancashire, where frequently large oak sugar-hogsheads can be procured, often more than a ton, and even 25 cwt. of ash is put in a cask, by means of a mechanical arrangement which slowly turns the cask, on a platform, round its axis, whilst a heavy ram goes up and down, gradually compressing all the contents of the cask. This tight packing is of importance chiefly for oceanic transport, where space, not weight, is paid for.

Since buyers require ash of different strengths, but the works only turn out one or two or, at most, three strengths, the task of *reducing stronger alkali to a lower degree* has frequently to be accomplished. This is mostly done by means of *common salt*, which must be deprived of its moisture (prejudicial to the grinding of the ash) by drying in a furnace till all water is driven off and the salt has decrepitated. The quantity required for reducing the ash is calculated, and added in grinding, by shovelling it up with the bulk of the ash beforehand and allowing both to be lifted up together by the elevator into the millhopper. Uniform mixing is required to avoid troublesome reclamations; and it is the more difficult the further the ash has to be reduced.

In England and Scotland, *kelp salt* is very often employed for reducing the ash, obtained in Glasgow as a by-product of the iodine-manufacturers. It consists principally of sodium chloride, but contains sufficient carbonate (probably also a little potash) to indicate from 8 to 12 per cent. available soda. Formerly kelp salt was so

cheap that the chloride cost nothing and even the carbonate cost a little less than the same amount of soda ash; hence it was gladly employed in the place of common salt, which had to be paid for. Recently it has become dearer, and even the chloride contained in it must be partially paid for; many alkali-manufacturers have accordingly given up using it, since the small advantage to be obtained by reducing the ash with kelp salt instead of with common salt is not sufficient to compensate for the increased risk of unequal mixing produced by the much larger quantity required for the mixture.

CHAPTER X.

THE PURIFICATION OF SODA ASH.

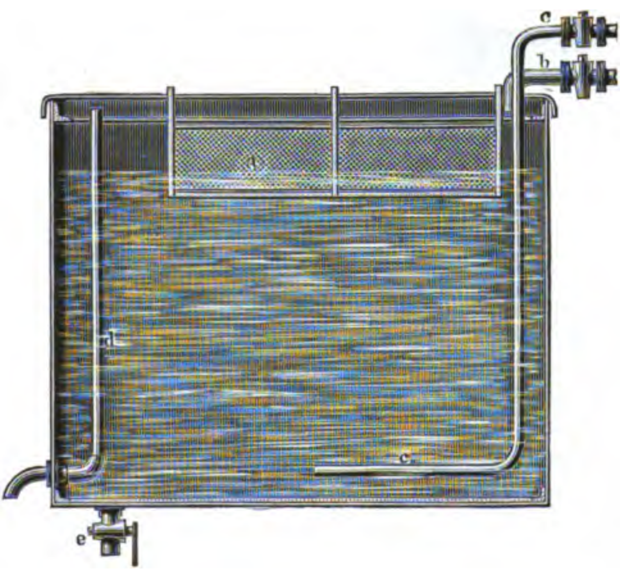
For many purposes the ordinary soda ash of trade ("yellow carbonate") is not pure enough; its caustic and especially its iron are troublesome, as well as the insoluble residue. This is especially the case where the ash must be employed as a whole, without previous dissolving and settling, *e.g.* in glass-making; and for the finest descriptions of glass, as well as for some other purposes, *refined or white alkali* is asked for. The soda can seldom be obtained sufficiently pure by boiling down and fishing from the tank-liquor; and the roundabout process of calcining the black salt and redissolving must generally be resorted to. The principal impediments to direct manufacture of pure alkali are the ferrocyanide (which, when once formed, can only be got rid of by calcining and converting into ferric oxide) and other insoluble substances difficult to avoid. Soda ash carbonated by gas is much purer than that carbonated by sawdust, and very rarely need be subjected to a refining process; but it is never quite so white as alkali refined by redissolving.

Accordingly the soda ash which undergoes refining is usually that which has been carbonated with saw-dust. In theory the process is extremely simple—viz. dissolving, settling, evaporating, and calcining; but in practice it demands great attention in order to furnish a product satisfying all the requirements of the buyers.

The soda ash is for this purpose employed unground, and is first *dissolved*. This is done according to various plans, identical with those employed in the manufacture of crystal soda; so that one description will do for both. Often, in small works, simple square

or round iron tanks (fig. 236) are used, in which a strong wire sieve, *a*, is suspended so that its bottom is below the level of the liquid; a water-pipe *b*, an open steam-pipe *c*, and a siphon or cock

Fig. 236.



complete the apparatus. For running off, the most suitable contrivance is a pipe, *d*, with an inner limb turning on a swivel which is ordinarily turned upwards, but for running off is gradually turned round and permits drawing off the clear liquid from the mud. A large cock, *e*, in the bottom serves for letting out the mud.

In the place of the simple turning pipe, or drop siphon, *d*, which consists of an ordinary gas-fitting, a more durable swivel joint may be employed, as shown in figs. 237 and 238, consisting of two cast-iron elbow pieces, *a* and *b*, the joining ends of which are ground into each other as a valve into its seat; these are kept together by the screw-clamp *c*. One of the elbows is connected with a short piece of pipe, *d*, attached to the side of the vessel; the other carries a longer upright pipe, *e*. Wherever in future drop siphons are mentioned, the above-described or a similar swivel joint may be employed.

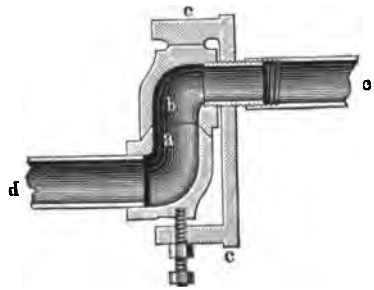


Fig. 237.

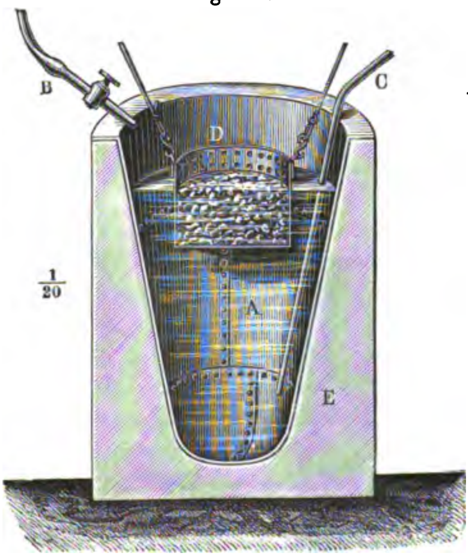
Fig. 238.

The tank is filled with water up to the height of the sieve (if warm water is at disposal for this purpose, so much the better), and steam is injected till the liquid boils; now the soda ash is gradually put upon the sieve and left to be dissolved. At the same time the boiling secures a good agitation of the liquid—which is always necessary, even with a suspended sieve, because much fine powder falls through this to the bottom. Soda ash is not quite so soluble in boiling as in tepid water; but this does no harm, as the liquid must of course cool down a little during the settling. Usually the liquor is made 54° to 56° Tw. strong, measured hot. Often during dissolving a little bleaching-powder made into a cream is added, say $\frac{1}{10}$ to $\frac{1}{4}$ per cent. of the weight of the ash; this has the twofold action of oxidizing any ferrous salts, of converting the sulphite into sulphate, and of destroying the organic, humus-like colouring-matter. The ferric oxide is at once precipitated by the soda as hydrate, and, in spite of its usual gelatinous form, is easily got rid of, as the equally precipitated calcium carbonate carries it down and causes it to settle quickly. Of course a quantity of soda corresponding to the bleaching-powder is converted into chloride; so that the strength of refined alkali is rather below that of the soda ash, although the insoluble substances have been removed. It is advisable, however, to employ from the first soda ash yielding a completely colourless solution (p. 532); for then no bleaching-powder at all need be used.

In France, in small works, soda ash is dissolved (for crystal-making) in deep conical boilers, A, fig. 239, which are sometimes heated by an open fire, but more frequently by steam. B is a water-pipe, C the steam-pipe, D a box of perforated sheet iron, which is suspended by two chains, and thus can more easily be

moved up and down and adjusted to the level of the liquid than the sieve in fig. 236, intended for a larger scale of working.

Fig. 239.

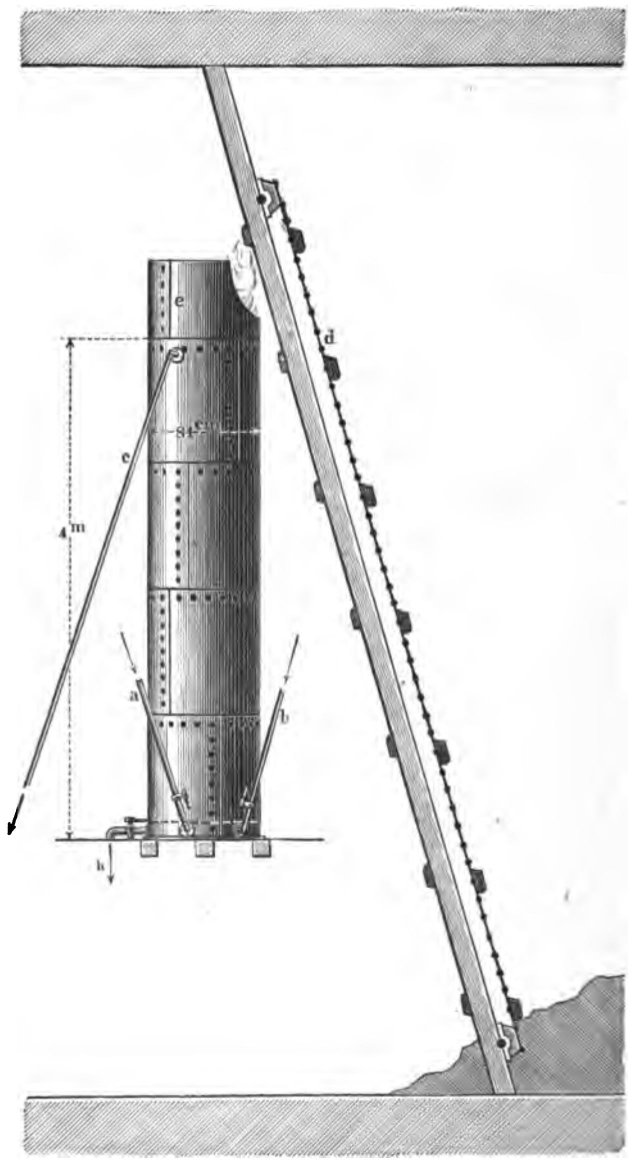


In larger works solution is mostly hastened by employing vertical iron cylinders with mechanical agitators, into which the soda ash is gradually charged after the water has been got up to the boiling-point. Such a vessel, 8 feet in diameter and 6 feet high, can dissolve 40 tons of soda ash in 16 hours. Hausamann (Dingl. Journ. ccxiii. p. 129) proposes injecting the steam through two cross branches at the bottom of the vessel, which will be automatically turned round by the impact of the issuing steam itself, the upper vertical pipe turning freely, being connected with the main pipe by a gland; chains dragging behind the cross-shaped pipe are continually to stir up the bottom mud. Sometimes semicylindrical vessels with a horizontal agitating shaft are used; these also are said to work very well.

A very suitable continuously acting dissolving apparatus, employed in a Swiss works, is shown in fig. 240. A sheet-iron cylinder, 13 feet high and 2 feet 9 inches wide, open at the top, closed at the bottom, and provided with a false bottom at but a short distance

from the true bottom, is entirely filled with soda ash. Below the false bottom enter both the water-pipe *a* ($1\frac{1}{2}$ inch) and the steam-

Fig. 240.

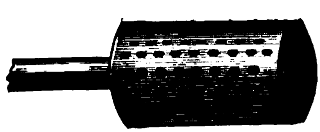


pipe *b* (1¼ inch). By these a solution of alkali is produced, which on rising in the cylinder is quite saturated and runs off at *c* through a 2½-inch pipe in this state; it is filtered through the ash in the cylinder itself. An elevator, *d*, constantly pours fresh soda ash into the top of the cylinder in the same ratio as it is dissolved; the piece *e* serves to keep the ash put on from falling down. The cock *h* (2½ inches) serves for discharging the whole apparatus when it is to be stopped or cleaned out.

When, in the ordinary construction, the necessary strength of the liquor in the dissolver has been attained, the steam is cut off, the agitator (if one be present) is stopped, and the liquor allowed to rest for a few hours; it is then drawn off as much as possible from the mud, preferably by the swivel siphon *d* (fig. 236), first of all into the settlers. The mud is sometimes left in the dissolver over several operations, according to its quantity; it must always be ultimately removed. It consists of calcium carbonate, aluminium silicate, ferric oxide, sand, &c., but always contains a large quantity of sodium carbonate mechanically absorbed. The simplest way of recovering the latter seems at first sight to be by putting the mud into the black-ash tanks; but it stops these up very soon and causes them to work irregularly; hence it must be lixiviated by itself, when it will also yield a purer liquor. This is effected by once or twice boiling up with water, settling, and decanting; the washings are employed for dissolving fresh soda ash. This operation is rather troublesome; it can be very much facilitated by employing either a filter press, or a filter made of porous material with a vacuum underneath it, similarly as in causticizing soda by lime.

The liquor coming from the dissolver must first of all be completely *settled*; upon a careful separation of all insoluble matters the success of the operation essentially depends. This is attained by 12 or 24 hours' rest and careful drawing off from the sediment. For the sake of safety the inner end of the running-off pipe can be surrounded by a perforated drum, fig. 241, covered with a double

Fig. 241.



envelope of closely-woven calico, through which the liquid will be filtered from any fine particles still suspended in it. Since in this case the whole of the sediment does not get upon the filter, it is not so easily stopped up as the ordinary filters, which are never met with in any large works, because they constantly give way.

A very good continuously acting clarifying process consists in passing the liquor slowly through long distances. If it is run into one end of a long and capacious vessel (say one half of a steam-boiler cut in two), the current slackens so much in the vessel, that, before running out at the other end, it has deposited nearly all suspended particles (similar to rivers flowing through a lake); and by once or twice repeating this process the liquor may be run off perfectly clear.

Of course under no circumstances must the settling operation be protracted till the soda begins to crystallize out. This does not easily happen, as the large bulk of liquid keeps warm for a long time. But it is advisable to surround the settlers with bad conductors of heat (wood, straw, brickwork, &c.). Since soda has its maximum of solubility at 38° C., nothing can crystallize out above that temperature.

The settled liquor must now be *boiled down*. This is done in any of the usual pans. On the Tyne, where most refined alkali is made, the liquor for this is boiled down with top heat, but always in pans heated by a special fire, preferably a coke fire, so that no flying ashes can get into it. Frequently pans of 24 to 27 feet length are employed, fitted with a coke fireplace at each end; the flames travel over the liquor, unite in the centre of the pan, and are here conveyed into a common flue leading to the chimney. Experience has shown that much less soot is formed thus than if the flame travels from one end along the whole length of the pan; but the utilization of the heat is very imperfect. The flame of the drying-furnace is not used for heating the pan (for which it would not in any case be sufficient), in order to avoid soot, and because the furnace itself would have to be fired with coke. The boiling-down is again continued till the consistency of mortar is attained, when the refined salt is drawn out into a drainer like that in fig. 171 (folding plate to p. 386).

Since it is difficult on making good the joints of the doors with clay or lime to prevent some of this getting into the drainers, those with slanting-out pockets (figs. 200 & 201) are preferred for

refining-pans. The mother liquors are always pumped back into the pan, and worked up with the next batch.

In other places bottom-fired pans of different constructions are employed; besides the usual descriptions, cast-iron pans of the shape of a segment of a sphere are also used, by which fishing is much facilitated; but they are liable to crack.

The fished or drained salt now need only be dried in a reverberatory furnace, and ultimately ignited strongly, of course not up to the fusing-point; last of all, it is finely ground and packed. All this is very simple work; there is no carbonating here; and fluxing cannot easily occur. But the greatest cleanliness must be observed; at large works there are always present a special room, a special mill, &c. for this manufacture.

Usually the loss in refining, through insoluble residue, incomplete washing, &c., is reckoned at 5 per cent. of the soda ash dissolved. The strength of the alkali is not sensibly increased, notwithstanding the removal of the insoluble portion; and if bleaching-powder be employed, it is even lowered by ½ or 1 degree, owing to the decomposition of sodium carbonate by calcium chloride.

Good *refined alkali* should be of perfectly white colour, without any yellow shade, and should show extremely few black spots; but very few descriptions are absolutely free from the latter. It must dissolve in water completely (without leaving any residue), forming a perfectly clear solution. Caustic soda ought not to occur in it at all, or at most only a small fraction per cent.; of sodium sulphide and sulphite, or of iron, it should not show even a trace. Analyses have been given on pp. 551 & 552.

The Manufacture of Crystal Soda.

In spite of the large quantity of water which has to be carried about in crystallized soda (100 parts of the latter consisting of 37·08 parts of sodium carbonate and 62·92 parts of water), and the further drawback that it is much bulkier and requires proportionately more packages for the same weight than soda ash, it is still manufactured in enormous quantities, not merely at the alkali-works themselves, but also, in the north of France and in Holland, by a number of manufacturers who buy soda ash and convert it into crystal soda.

The reason why this product can bear the increased cost of

carriage, packing, and manufacturing, is partly because it is purer than any other form of sodium carbonate obtained on a large scale (and this purity is shown even outwardly by its crystallized state), but more especially on account of its freedom from iron and insoluble substances. For this reason, in some branches of industry they regularly use soda crystals, even when soda ash might just as well, and more cheaply, be employed. But the principal consumption of crystal soda is for domestic purposes, viz. for washing. Here it is a most important circumstance that crystal soda is quite free from caustic and other compounds acting similarly on the skin (sodium aluminate and silicate); so that the hands of the washerwomen suffer less from it. Moreover it is more easily divided and handled than the finely-powdered soda ash, which on lying exposed to air (especially to the air of a wash-house) cakes together into lumps; and, above all, it is easily dissolved in water, whilst soda ash would partly remain as a hard lump at the bottom of the wash-tubs, and some grains of it would get mixed up with the clothes, and injure them in some cases. Hence soda ash is never employed in washing, but always crystal soda; and this readily accounts for the enormous scale on which the latter is manufactured. It is frequeutly sold under the commercial name of *washing-crystal.*

Although for most applications of crystal soda a faintly yellow colour, produced by organic substances, would not do much harm, still in the trade as colourless an article as possible is always asked for, and that justly, since only this affords to the consumer a sufficient guarantee of its freedom from sulphide, iron, &c. Hence, till quite recently, notwithstanding very numerous endeavours, crystal soda was not made direct from the tank-liquors by a single crystallization. A few manufacturers, by very thoroughly carbonating with gas and very long settling of the tank-liquor have succeeded in making white crystals from it; but these are complained of as being too soft and not easily saleable; and in most places their preparation has been considered too troublesome. There is, however, more prospect now of making good crystal soda directly from the purified tank-liquors obtained by the Pechiney-Weldon process.

Crystal soda (on the Tyne usually called simply "soda") is accordingly practically always made from previously calcined soda ash (yellow carbonate) by *dissolving* it at a higher temperature and

allowing it to *cool* in iron vessels. Sometimes it is stated that for this purpose an impure soda ash, otherwise not saleable, may be taken; but this is decidedly wrong. If such ash is of very low strength, the quantity of mother liquor will be much larger. If it is coloured by iron, this does not do much harm, as the ferric oxide remains behind; yellow or even reddish soda ash often yields better soda crystals than white ash, whose better colour is sometimes owing to incomplete oxidation of the iron. Above every thing the soda ash should be nearly free from caustic soda and unoxidized sulphur compounds; not only are these themselves uncrystallizable and increase the quantity of mother liquor at the cost of the yield of crystals, but they prevent the perfect settling of the liquor, and, even after filtering, impart to it a colour which is found again in the crystals, and which no doubt is due to organic substances dissolved by the caustic or sulphide. The latter fault can sometimes be corrected by means of bleaching-powder; but in this case a corresponding quantity of sodium carbonate is lost, and sometimes the smell of the chloride obstinately adheres to the crystals. In English works with well-carbonated ash about $\frac{1}{8}$ by weight of bleaching-powder per cent. of the crystal soda is used. In French works sometimes lead sulphate is employed, here and there in combination with bleaching-powder. Badly carbonated ash containing much organic matter, especially when made with the help of sawdust, will often not yield a clear solution at all, at any rate not one of high concentration. Consequently for crystal-making the quality of the soda ash ought to be carefully attended to. Ash that colours by lying in the air is not well adapted for it. The French makers of crystals require the maximum of caustic contained in the soda ash to be 1 per cent.; the ash is then sure to be free from sulphide and organic matter, since only by excellent calcining can the above point be reached.

The *dissolving* is done in precisely the same way and up to the same strength (52° to 61° Tw.) as has been described when treating of refined alkali (p. 556 *seq.*). Exceptionally, dissolving by steam has been proceeded with only to a strength of 45° Tw., followed by settling, boiling down over a direct fire to a strength of 58°, and running into the coolers. This yielded a very fine quality, but has been given up on account of the expense. In a large English factory the liquor, hot from the dissolver, showed 60° or 61° Tw.—in the settlers at 35° C., 66° or 67° Tw.

Not quite so much care is taken in settling the liquor for crystals as for refined alkali, since the suspended impurities subside in the coolers before crystallization sets in, and consequently can be mechanically removed from the crystals. Sometimes no other settling takes place than that in the dissolvers; in large works, where the dissolvers have to go on continuously, at least two special settlers are employed, which are used alternately, and in which the liquor remains twenty-four hours. From these the liquor is run into the *coolers* or *crystallizing-cones*. These in England are always very large, in France very small, and in Germany usually of a medium size. The large cones are mostly made of cast-iron, frequently in the shape of segments of spheres, about 9 feet in diameter and 2 feet deep, cast 1 inch thick; each such cone yields from 20 to 25 cwt. of crystals. But pans and vessels of other shapes, both of cast and of wrought iron, and of very various sizes, are employed.

The shallower the coolers are, up to a certain limit, the better; thus wrought-iron vessels 20 feet × 6 feet and 2 feet 2 inches deep have turned out very successful. The cast-iron pans sometimes used in Lancashire, 6 feet in diameter and 2 feet 6 inches deep, are already too deep. On the Tyne and Clyde the shape adopted by the largest works is an oblong with rounded corners, with a bottom sloping to one side, and in it an outlet-opening for mother liquor (figs. 242 & 243). The bottom is so shaped that the whole

Fig. 242.

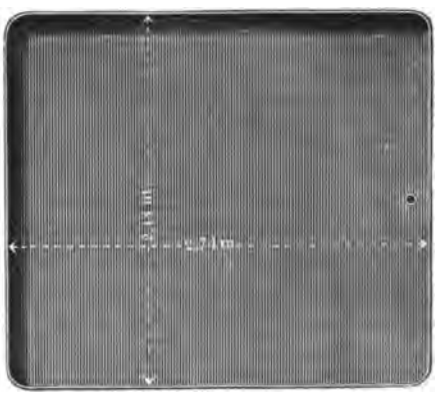
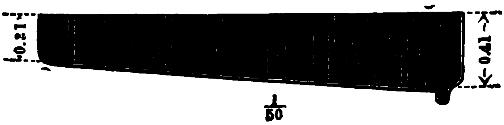


Fig. 243.



of the mother liquor can run out through the opening. A cone of the size represented weighs from 42 to 43 cwt, and yields 28 cwt. of crystals in seven days.

The cones are placed in rows in a large shed, which in summer is always kept very airy by means of open lattice-work; between each two rows there runs a gutter along the bottom for the mother liquor, and above the cones a spout of thin cast iron with openings in the bottom for the cones. These openings are continued into short valve-seats, usually closed by ground-in cast-iron plugs; and each of them, by means of branch spouts, can feed several cones. It is advisable to lay the whole floor with flags in cement or with asphalt, so as to have from each side a fall towards the centre; here all spilt liquor collects in a well placed at the deepest point. Sometimes, where space is an object, two or even three floors of such cones are placed under one roof.

The cones are filled nearly to the top, and several strips of sheet iron laid over them at right angles to each other. Crystallization sets in first upon these; and soon a complete crust of crystals is formed, which grow downwards into the liquor, often to more than a foot in length, and yield the finest article. Less fine are the crystals formed on the sides, which have to be cut off with chisels; least fine are those formed on the bottom. In order that the crystals may not be contaminated with iron, the cones must be kept bright and free from rust; sometimes they are painted (p. 169).

In cones holding a ton and upwards the crystallization is finished in from 6 to 8 days in winter, in 14 days in summer; but of course in summer, even with longer waiting, the yield is smaller, since more soda remains dissolved in the mother liquor. In warmer countries, as in France, the manufacture must be entirely discontinued in summer. When the cooling is complete the upper crust is broken and the mother liquor drawn off by a siphon. If the vessel has an outlet through the bottom, which in the meantime had been closed by a wooden plug reaching above the level of the liquor, this is

loosened by a few blows with a hammer, pulled out, and the liquor run out completely. Then the crystals are broken off, drained within the cone itself, and put on a wooden bench inclined a little forward, where they partially dry in the air for 24 hours; they are then packed in casks. Sometimes they are even packed directly after draining in the cones.

In France regularly, and sometimes in Germany, much smaller vessels are employed, even in large works where thousands of them are required. In that warmer climate they seem to answer better than the large English cones. And the wages do not seem to amount to much more: *e. g.* in a works in the north of France they are stated to be 37 centimes per 100 kilog. against 35 in Glasgow, which statement certainly does not take into account the generally higher rate of wages in the latter place. The soda ash is dissolved in apparatus of manifold shapes, sometimes subsequently concentrated by high-pressure steam, cleared with the assistance of lead sulphate or bleaching-powder, and drawn off with an india-rubber siphon, by which a large number of the vessels can be filled very quickly. These are mostly of cast iron, in the shape of very thin pots of 14 to 18 inches diameter and about 8 inches depth. They are placed on wooden stands, a number of tiers one above another. The crystallization takes 24 or, at most, 48 hours; then a hole is broken in the top crust, the mother liquor poured off by tilting the pots on one side and leaning them against a lath, on special draining-stages with troughs running underneath.

The cakes of crystals very firmly adhering to the sides are detached by holding the pots for a moment in a hot-water pan, or even in the steam arising from it: the layer in immediate contact with the sides melts; and then the whole cake can be tilted out. The loose cakes are again drained for 24 hours, standing on edge in many rows, leaning against one another; they are then broken into pieces, and these exposed in stoves on wooden shelves to a temperature of little more than 20° C. till they are quite dry and just begin to effloresce at the points. Then they are at once packed close, to prevent any further efflorescence.

Other works employ boxes of very thin, pliable sheet iron 2 feet 3½ inches long, 12 inches wide, and 9 inches deep, with strengthened edges and with loops for easily handling them. These also are put in several tiers one above another, and are finished in 24 to 36 hours. After pouring off the mother liquor, the crystal cake can

be easily detached, owing to the elasticity of the sides and the bottom. The further treatment is as above described.

In Germany crystallizing-vessels in size between the French and English are mostly used.

Brown states the composition of two samples of soda crystals as follows :—

Sodium carbonate	36·476	36·931
„ sulphate	0·943	0·542
„ chloride	0·424	0·314
Water	62·157	62·213
	100·000	100·000

The *mother liquors* from the crystals still contain a great deal of sodium carbonate, and the more the higher the temperature of crystallizing. Besides, they contain all the caustic and most of the chloride and sulphate, of which mostly less than 1 per cent. crystallizes along with the soda. Such a mother liquor, of spec. grav. 1·2131, showed the following composition :—

Na_2CO_3	8·20
NaOH	4·30
NaCl	3·30
Na_2SO_4	3·08
Fe_2O_3 and Al_2O_3	0·23
Water	80·89
	100·00

These mother liquors are boiled down in pans to the consistency of mortar (in one works the cylindrical pan with side pockets, described on p. 514, is employed for this purpose), and calcined in a furnace; they yield a very white alkali, but of course of lower strength. This *mother-alkali* in winter shows 30 per cent. available soda, and in summer, according to temperature, from 40 to 45 per cent. In the north of France an average of 55° Descroizilles is reckoned. It is principally used in glass-making, where the sulphate contained in it is utilized. Its quantity varies according to the season.

Exceptionally an impure crystal soda is recrystallized by melting

it in an open pan by means of direct fire, with the addition of a little water and milk of lime or bleaching-powder, and, after settling, running it into the coolers. Under ordinary circumstances this would not pay.

The *yield* can be seen from the following figures, obtained from actual practice. 1700 tons of 52-per-cent. soda ash yielded 3250 tons of crystal soda net weight, or 3533 tons gross weight *, besides mother-alkali of varying strengths, equivalent to 347½ tons of 48-per-cent. available soda.

Another trustworthy statement, from an English works, puts the yield from 100 tons of 52-per-cent. soda ash, deducting the mother-alkali (*i. e.* not including it in the 100 tons), at 233 to 237 tons of crystals. The mother-alkali amounted, upon 1000 tons of crystals, to 110 tons of 36½-per-cent. =80·7 tons of 48-per-cent.

At a French works, on 100 crystals 6 mother-alkali of 55° Descroiz. is reckoned.

Some crystals are often *adulterated* with the much cheaper Glauber's salts; just those consumers for whom the latter is absolutely worthless, viz. housewives and laundresses, are most exposed to this fraud. J. H. Swindells (Chem. News, xvi. p. 227) mentions that the manufacture of mock Scotch soda crystals was carried on on a large scale, and the product sold as "best Scotch soda" (comp. p. 169).

* On the Tyne crystal soda is sold by gross weight, without taring the casks, which makes a difference of 7½ per cent. compared with net weight. This is done to save the taring of casks and the complication of invoices, too troublesome for such a cheap article.

CHAPTER XI.

BICARBONATE OF SODA.

The properties of this salt and its solutions have been described above on p. 283, in connexion with the other carbonates of sodium. Its preparation, so far as it belongs to the ammonia-soda process, will be described in that Chapter, since in that case the bicarbonate is essentially a transition stage, and rarely comes into the trade as such, owing to the difficulty of entirely depriving it of adhering ammonium salts without losing any carbonic acid.

Richards, on Jan. 29th, 1874, patented the process of treating 1000 parts of the sodium bicarbonate, made in that process, with a mixture of 3 parts liquor ammoniæ with 150 parts water, in order to convert the ammonium bicarbonate into monocarbonate and washing out the latter. But in practice nearly all commercial bicarbonate is still made by treating crystal soda with carbonic acid.

On a small scale this is done by passing CO_2 into a cold saturated solution of sodium carbonate till the bicarbonate, owing to its lesser solubility, is precipitated. On a manufacturing scale the CO_2 is always made to act upon solid crystal soda, for which the inferior yellowish crystals may be taken without injuring the quality of the bicarbonate.

The *carbonic acid* is obtained from various sources. In some places natural eruptions of that gas occur, which are collected in a kind of wells, washed, and conveyed into the absorbing-vessels. Elsewhere the CO_2 of fermentation is used for this purpose. Formerly, when Epsom salts could not be made so cheaply as now (from kieserite), their manufacture was sometimes combined with that of

bicarbonate, by dissolving magnesite in sulphuric acid and utilizing the escaping CO_2.

The gas obtained on burning lime (comp. Chap. XVII.) or coke is sometimes employed for bicarbonate, but is not very well adapted for this purpose, and never yields a first-class article, being too impure, too hot, and charged with soot, ashes, &c. These drawbacks might be mostly remedied by cooling and washing; but the great dilution of CO_2 by N &c. cannot be avoided, and hence a salt saturated with CO_2 cannot be obtained. Neither has the production of CO_2 by the action of superheated steam on limestone turned out successful for this purpose.

Although perhaps here and there a little bicarbonate may be made in other ways, the principal seat of its manufacture is in English works, where the carbonic acid is made from limestone and hydrochloric acid, which is said to have been done first by Schoeffer in 1840. This is principally done in factories which, owing to the arrangement of their furnaces, produce large quantities of weak muriatic acid (1°–7° Tw.), for which to this day no other outlet of any importance has been found. Their apparatus is a large, tightly covered tank, made of stone flags, similar to a chlorine-still or in a rather simpler way, frequently sunk in the ground and surrounded by puddled clay. This tank is filled with limestone or chalk, and the muriatic acid run in by a pipe reaching nearly to the bottom, the CO_2 escaping through a pipe fixed in the top. A little below the top is an overflow-pipe, through which the solution of calcium chloride formed runs off when the level of the liquor has risen to that height; and from this moment the work goes on continuously, the supply of muriatic acid at the bottom being regulated so that it is entirely saturated before it gets up to the overflow. Thus it is only necessary to put in limestone from time to time, and to clean out the tank now and then from mud.

The crystal soda is exposed to the action of carbonic acid in apparatus of all shapes and made of various materials. Wood (rarely), brickwork, or, preferably, wrought iron is employed for these chambers; in any case they must be air-tight. If brickwork be used, a barrel arch with a flagged bottom is the best shape; the bottom is inclined from the sides to the centre, to collect the mother liquor. The iron chambers are often old waggon-shaped steam-boilers, or any other large reservoirs. They are frequently made large enough to walk about in. Otherwise their shape is of no importance. Some-

times they hold as much as 60 tons of crystals, and yield 30 tons of bicarbonate. Mostly they are connected in such a way that the gas passes from one chamber to another and is thus used up systematically; the fresh gas always enters the oldest chamber first, and arrives last at the last-charged chamber. The entrance doors must be tight; and sometimes the joints are plastered with clay. Since, during the absorption of CO_2, in spite of the liquefaction of the water of crystallization, much heat is liberated, which may injure the process, iron chambers, radiating the heat away quickly, are the best. Shelves are sometimes fixed inside, to receive the soda; at the large works these are dispensed with, the chambers being entirely filled in regular layers with blocks of crystals 4 to 6 inches thick, as they come from the sides of the cones. Sometimes by means of laths or boards a space of about 12 inches height is reserved at the bottom, into which the CO_2 enters and spreads all over, and the liquor collects; the outlet for the gas is always on the top.

During the action of the carbonic acid much water is liberated, according to the equation:

$$Na_2CO_3, 10H_2O + CO_2 = 2NaHCO_3 + 9H_2O.$$

This water remains saturated with salts, and especially takes up almost entirely the small quantity of chloride and sulphate accompanying the crystal soda, as well as any colouring-matters. The solution mostly runs off continually through a U-shaped pipe in the chamber-bottom, which prevents the gas from getting out. The stoppage of this running proves that the end of the absorption is near at hand, which in large chambers usually takes from six to nine days. The following indication is certain:—A man pushes a strong bar of iron through a hole (otherwise closed) in the chamber-side into its interior; only when the bar gets as far as the centre of the chamber without meeting any hard crusts of soda is the bicarbonate finished. A certain test is furnished by dissolving a sample from the interior in water and adding mercuric chloride, which ought not to produce a yellow precipitate, but only a white cloudiness.

When the absorption is finished, the current of gas is interrupted, the door opened, the chamber aired and discharged. The soda crystals are found converted into bicarbonate without a change of form—that is, as pseudomorphs. The salt, however, is still very damp, and must be dried. This is done in stoves, filled entirely or

on several shelves, and heated by hot air or steam-pipes to 40° or at most 45° C. A current of carbonic acid of the same temperature would be better, but is too expensive. Aspirating fire-gases by a fan-blast or chimney has been tried, cooling them down to the above temperature, and depriving them of soot and ashes by fine wire sieves; but the desired snow-white colour of bicarbonate cannot be attained in this way. The drying often lasts eight or ten days. The bicarbonate amounts to about 50 per cent. by weight of the soda crystals, to more if the latter have effloresced—in which case the conversion into bicarbonate takes place more easily and quickly. The dried bicarbonate is ground, in mills similar to ordinary corn-mills, to an extremely fine powder, and sifted through a sieve with about 20 holes to the linear inch. Great care must be taken in grinding that the mill does not get too hot, lest the bicarbonate lose some of its carbonic acid. Even during long keeping in the warehouse, worse in the open air, a little CO_2 escapes. It is mostly packed in casks holding exactly 1 cwt. (net weight).

From the *mother liquor* running off, by drying down and calcining, refined alkali of 36 per cent available soda is obtained. This liquor, owing to its bicarbonate, is very well adapted for desulphurizing tank-liquor, but rather diminishes the alkalimetrical strength of the latter by its chloride and sulphate.

Mohr has proposed to avoid the formation of any liquor by mixing 1 part crushed crystals with 3 parts calcined soda ash, and exposing this to the action of carbonic acid. This is not a practical process: too much heat would be set free, which in large masses might redecompose the bicarbonate formed; moreover calcined soda ash is much more impure than crystals, and the further purification by the mother liquor running off would not take place.

Examination of Bicarbonate.—Since this article is nearly all consumed in medicine and in the preparation of food, a higher degree of purity is justly demanded for it than for merely technically applied chemicals. Bicarbonate occurs in the trade in very white crusts, stable in the air, devoid of smell, very dense and crystalline; and the English article occurs as an extremely finely ground powder. The latter, even on standing for a time in the air, loses a portion of its CO_2, while the crusts are more stable. It must form in water a perfectly clear solution, and after acidulating produce only very slight opacity with barium chloride and silver nitrate. It must be absolutely free from metallic impurities indicated by sulphuretted

hydrogen or ammonium sulphide. All these conditions are very easy to fulfil, more so than that of avoiding any admixture of mono- or sesquicarbonate. The presence of these is proved qualitatively by the reddening of turmeric paper, by the cold solution of the bicarbonate producing an opacity on pouring it into a solution of magnesium sulphate, or by a yellow precipitate with a solution of mercuric chloride. Pure bicarbonate, dissolved in 15 parts water, with a solution of $HgCl_2$ in 2 parts water should show a white cloudiness only after the lapse of a few minutes, and only gradually turn brown.

In trade an actual estimation of the carbonic acid is asked for. Theoretically bicarbonate contains 52·37 per cent. CO_2, in practice 50 per cent. is considered sufficient. The estimation at the works is nearly always made by one of the modifications of the Fresenius-Will apparatus for driving off the CO_2 from the dry salt and ascertaining the loss of weight. The inverse method, titrating the soda alkalimetrically, is not trustworthy, because all the foreign salts would then be calculated as bicarbonate. Another plan is to dissolve the salt, adding calcium chloride and ammonia, boiling, filtering of the calcium carbonate, washing, and titrating it alkalimetrically. Or standard baryta solution is added for precipitating all CO_2, the liquid poured through a dry filter, and the excess of baryta retitrated in an aliquot portion of the liquid. All these plans have the drawback that all sources of error influence the small apparent proportion of monocarbonate either by increase or diminution. Hence Mebus (Dingl. Journ. ccxiii. p. 64) proposes weighing off two equal quantities of substance, titrating one alkalimetrically, and adding to the solution of the other an exactly corresponding quantity of standard caustic soda, free from carbonic acid; now a quantity of caustic soda, corresponding to the monocarbonate originally present, will be left over in the free state, and can be estimated by adding barium chloride, filtering through a dry filter, and titrating an aliquot portion of the filtrate.—The only plan mentioned in Payen's treatise, p. 482, is probably but little employed, and not very much to be recommended: 5 grams of the salt are to be heated and the CO_2 expelled, collected in a graduated tube over water covered with oil. 5 grams of pure bicarbonate at 0° C. and 760 millims. pressure would yield 657 cub. centims. of carbonic acid gas.

Applications of Bicarbonate.—Most of it is employed, more in

America than in Europe, as baking-powder. It is also extensively employed medicinally as a remedy for acidity of the stomach and calculus; Bullrich's salt and Tomlinson's milk powder are common bicarbonate; Seidlitz powders &c. contain it as an essential constituent; Ems, Vichy, or soda-lozenges are nothing but this salt mixed with sugar and compressed into small cakes. It is also employed for making effervescent drinks on a small scale. In housekeeping it serves as baking-powder, for taking away the acidity of milk and of some other articles of food, for making hard water better adapted to making tea and boiling peas &c. In laboratories it is used as a convenient and cheap means of preparing pure sodium carbonate. It has but few technical applications in the proper sense, *e.g.* for gilding and platinizing, sometimes for scouring wool and ungumming silk, and for filling the "extincteurs." The proposals to employ this salt, along with sodium sulphide &c., for manufacturing alkali have been described in another place.

The Manufacture of Precipitated Sulphate of Lime (Pearl Hardening).

The above-named article (in Germany known as "annaline") is used by paper-makers as an addition to half-stuff. It is hydrated sulphate of lime in a peculiar state of crystallization, specially suitable for this purpose. It is made in one works at least as a by-product of the manufacture of bicarbonate, by adding sulphuric acid to the calcium chloride solution which would otherwise run to waste. It contains a little free hydrochloric acid, and therefore is first completely neutralized by slaked lime, a slight excess of which does no harm. The muddy liquor is cleared by settling, and, in a wooden tank lined with gutta percha, diluted to 15° Tw. Its volume is gauged here, and an exactly equivalent quantity of sulphuric acid of 46° Tw. run in from another gauged tank. The two liquids are well mixed; calcium sulphate falls down at once; and the whole is run through a plug-hole onto the filters. These are also made of wood and lined with gutta percha, with a boat-shaped bottom. On this some bearers are laid, reaching up to the straight part of the vessel; across these 1-inch laths, a quarter of an inch apart, form a grating, which is covered by a piece of calico, kept down at the edges by strong laths. These filters work well, and need not be cleaned out very frequently; the liquor runs away from

them through a gutta-percha pipe; and in two hours they are dry. The precipitate is then washed for three hours with clear, filtered lime-water, without stirring it up. These washings run into the limestone cisterns along with the other weak acid. The washed mass is taken out, put into canvas bags, and pressed in cylindrical presses, which are lined with brass fluted lengthways for the better running-off of the liquor. The pressing is done by manual labour. The pressed cake is cut up into square pieces and sent into the trade; the substance in this state still contains 40 per cent. of water.

CHAPTER XII.

YIELD AND COSTS.

The *yield* in alkali-making is very much below that required by theory. 100 parts of pure Na_2SO_4 ought to yield 74·65 pure Na_2CO_3 or 43·66 Na_2O. Even 96-per-cent. sulphate ought still to yield 71·66 per cent. pure Na_2CO_3 or 41·91 per cent. available soda. But the *highest* actual yield of the *best* English works (if none but statements of a thoroughly trustworthy character be accepted) from 96-per-cent. sulphate very rarely exceeds 69 to 70 per cent. of 52-per-cent. soda ash—that is, 35·88 to 36·40 Na_2O, instead of 41·91. Even in factories working with revolving furnaces and obtaining very strong alkali, the author knows of no higher maximum than 36·5 Na_2O. This was but rarely reached; and neighbouring managers attributed it to giving "very good weight" of sulphate in the balls. On the other hand, he knows of cases where only 65 parts of 51-per-cent. ash were obtained, = 33·15 Na_2O. The best of these cases represents a loss of 12·2 per cent. of the soda; the worst, one of 20·9. A yield of 35·8 parts of available soda from 96-per-cent. sulphate, *i. e.* 85·7 per cent. of the possible soda, or a loss of 14·3 per cent., must be called a *very* good average result for English factories; it is equal to 69 parts of 52-per-cent. ash. Some manufacturers deceive themselves by making out higher yields, without checking how much less the sulphate weighs than it ought; for it is one of the most usual "dodges" of foremen to give a little extra weight of sulphate for each ball, so as to make a show of a good yield. Hill (Chem. News, xxx. p. 37) states it as a not unusual case that 2 to 6 per cent. sulphate over and above the nominal quantity is balled; and the author has personal knowledge of some cases of this kind. One of the best-

managed and most recently erected English works has an average yield on the sulphate of 73·5 per cent., calculated as 48-per-cent. ash, equal to 35·28 per cent. Na_2O, or 15·8 per cent. loss. This was the quantity as weighed into the warehouse; but a further loss of 2¾ per cent. of the total weight came out on adding up the invoice weights and deducting the salt added for reducing the ash. A portion (about 1 per cent.) of this last loss is accounted for by the trade custom of not paying for or invoicing the fractions of degrees above the integral numbers; the remaining loss is attributable to loss in grinding and the inevitable differences between weighing into and out of stock. A few years later the same works got up to 73·9 per cent. of 48-per-cent. ash, = 35·47 per cent. of Na_2O (=14·9 per cent. loss). This is the yield on the sulphate, that on the salt was 81·35 per cent. One of the best-managed Lancashire works obtains 71 per cent. on the sulphate, calculated into 50-per-cent. ash (actually as 52–58-per-cent. ash); this is equal to 35·5 per cent. Na_2O, or almost exactly the same as the last. By the Pechiney-Weldon process a yield of 78·68 per cent. of 48-per-cent. ash (Liverpool test) on the sulphate is obtained.

According to Landolt (Hofmann's Bericht, 1875, i. p. 422), the average yield of Na_2CO_3 in German works, on pure sulphate, is 64 per cent., which equals 37·43 per cent. Na_2O, or, calculated on 96-per-cent. sulphate, 35·9 per cent., which is rather more than the above-quoted English figures. But this estimate is above the truth, judging from the following figures, supplied to me by Mr. Schaffner, of the Aussig works (than whom probably no other continental manufacturer will do better), based on the very pure salt from Neu-Stassfurt, which tests regularly 99 per cent. of real NaCl:—

100 salt yield	120 sulphate.
100 sulphate yield . . .	150 black ash.
100 soda ash (53°) require	214 „ „
100 „ „ „	142·6 sulphate.
100 „ „ „	118·8 salt.
100 sulphate yield . . .	70 soda ash, 53°.
100 „ „ . . .	63 pure sodium carbonate.

The statements of Mactear (*infrà*, pp. 583, 584) should also be compared here.

The causes of this considerable loss, as compared with the theoretically possible results, are very numerous, and have been discussed by Hargreaves (Chem. News, xv. p. 219), Wright (*l. c.* xv. p. 259), Mactear (*l. c.* xxv. p. 54), and especially, with positive experiments, by Scheurer-Kestner (Compt. Rend. lxx. p. 1352, lxxv. p. 1184). They may be reduced to the following points :—

1. *Mechanical carrying-away of salts into the flues and the chimney.* This is proved by the presence of sulphate in the flues both of the black-ash and the carbonating furnaces.

2. *Volatilization of sodium compounds.* Wright estimates this loss at 1·14 per cent. of the total sodium (probably inclusive of No. 1). It will be so much the higher the hotter the furnace goes; and for this reason alone the men ought not to be allowed to work at a greater heat than necessary. It is not possible that the temperature of the furnace should usually be above the point of volatilization of sodium carbonate and sulphate; but by a rapid current of hot gas they might be volatilized in the melted state below their boiling-point, similarly to water. Scheurer-Kestner has examined this point more closely. He rejects the assumption of several chemists (Unger, Stromeyer, and others) that metallic sodium is volatilized in the black-ash furnace, an assumption which has now become entirely untenable by F. Fischer's analyses of the gases from black-ash furnaces (Deutsch. chem. Ges. ix. p. 1559), in which he always found an excess of oxygen. Usiglio, in exact experiments at the Chauny works, could trace the whole of the sulphur in the products; and error, he thinks, was all the more effectually excluded, as calcium and sulphur could equally be completely traced. On the other hand, Stohmann (Stohmann-Kerl's Techn. Chemie, v. p. 353), in exact experiments, out of 100 parts of sulphate balled in hand-furnaces could only trace 97·72, and if balled in revolving furnaces 99·53 in the products. That a certain loss always takes place in the black-ash furnace is positively proved by the flue-dust (which often contains from 50 to 60 per cent. of sodium sulphate), by the contamination of the liquor when boiled down with top heat, by the glazing of the furnace-bricks, &c. Hence Wright's and Stohmann's statements seem to deserve more credit than those of Usiglio, quoted by Scheurer-Kestner, according to which every kilogram of the sulphate charged is recovered in the black ash.

3. *By combination of soda with the materials of the furnace.* The furnace-bottom, especially, absorbs soda; this, however, in the

course of the year does not amount to a large fraction per cent. More is lost if fluxed black ash is allowed to run through the fire-bridge into the ash-pit.

4. *Incomplete conversion of sodium carbonate into sulphate.* This loss varies very much, according to the way in which the balling process is carried out. Hargreaves estimates it at a minimum of 2·19, or a maximum of 9·22 per cent. of the sulphate; Wright at 3·49 per cent., Mactear at 1·53 per cent. With cylinder furnaces it is mostly below 1 per cent. Too small an amount of coals or chalk, too much or too little heat, and bad work especially, raise this loss.

5. *The formation of insoluble sodium compounds.* It was known long since that the more ash is contained in the mixing-coal the less alkali is obtained—insoluble double silicates of sodium, aluminium, and calcium being formed. To this the bricks of the furnace contribute, as well as the (slight) percentage of alumina and silicate in the sulphate and the limestone. Wright estimates the loss from this source at 5·44 per cent. of the soda. But the principal researches on this point we owe to Scheurer-Kestner. He first proved distinctly that the principal cause of the formation of insoluble sodium compounds is the limestone, of which in ordinary black-ash furnaces much more than an equivalent is used. In a series of comparative experiments with the same charging-materials, he found that, on employing for 100 Na_2SO_4 only 95 $CaCO_3$, the tank-waste contained from 0·35 to 0·41, on the average 0·39 Na, but with

98	parts of limestone	0·59 per cent. Na.
102	„ „	0·86 „
107·5	„ „	1·27 „
111	„ „	1·30 „
112	„ „	1·36 „

Hence the quantity of the sodium remaining in the tank-waste increases proportionately to the limestone employed; and it is hardly possible to assume any thing else but the formation of an insoluble double carbonate of calcium and sodium, along with silicates. Scheurer-Kestner further proved that it is especially the calcium hydrate that retains considerable quantities of sodium carbonate (in direct experiments 4·95 and 4·75 per cent.), whilst it acts very little on caustic soda. It thus appears as if the lime on dissolving, when passing over into hydrate and acting on the dissolved sodium carbonate, converted a certain quantity of the latter

into an insoluble substance. This opinion of Scheurer-Kestner's is confirmed by the fact that a similar loss of insoluble soda is noticed on causticizing soda by quicklime, and also by the fact that in Mactear's cylinder-process (p. 419), where only the theoretical quantity of limestone is added, less insoluble soda is found in the residue. It must not be forgotten that, according to experiments by E. Kopp, Stromeyer, and the author, a portion of the sodium in the tank-waste is in the state of an insoluble ferro-sodium sulphide; this will increase with the iron contained in the mixing-materials.

6. *Incomplete lixiviation of black ash.* Even of the sodium-salt present in a soluble form a portion is always left behind in the tank-waste (p. 479). In the best case the soluble Na_2O amounts to 0·1 per cent. of the weight of the waste, *i. e.* about 0·45 per cent. of the whole available soda present; but with bad lixiviation this amount is increased ten- or fifteenfold; in Lancashire, where the lixiviation is frequently not as good as it ought to be, Wright estimates it at 3·61, Mactear at 2 or 3, per cent. of the soda. Variations will be produced by the quality of the black ash and by its treatment in lixiviation. We have previously seen what influence the porosity of the black ash has upon the lixiviation, and that the increased employment of revolving furnaces has long been retarded by the insufficient porosity of the balls made in them. Scheurer-Kestner found that of two sets of balls, which after grinding up left an almost precisely equal amount of soda in the waste, in actual manufacture (*i. e.* without grinding) one (the more porous description) left 27 per cent. less soda in the waste than the other (the dense one). Stohmann (*l. c.*) found the loss from this and the previous source together = 8·61 per cent. for hand-furnaces, 4·14 per cent. for revolvers, of the total soda.

7. *Formation of other sodium compounds not subsequently converted into carbonate,* especially sulphide, cyanide, sulphocyanide, ferrocyanide. Much more important than this is the

8. *Re-formation of other sodium compounds during the keeping of the black ash or during lixiviation.* We have seen, in the 7th Chapter, that by the influence of the atmospheric oxygen, and also by the mediation of ferric oxide, the calcium sulphide is oxidized and calcium sulphhydrate, polysulphide, hyposulphite, sulphite, and sulphate are formed, all of which on lixiviation decompose each its equivalent of sodium carbonate. This takes place especially when

the partially lixiviated black ash in the tanks is exposed to the air in the damp state. We have also said what is necessary on the influence of temperature, the duration of the lixiviating process, &c. This explains why the 3 or 4 per cent. of sulphate which soda ash should contain at most according to the laboratory test of black ash, in practice (except with cylinder furnaces) mounts up to 7 or 8, sometimes to 10 or 11 per cent. The loss from this source is stated by Mactear at 2·68 per cent., as the average of a series of experiments.

9. *Action of the lixiviating water*. This loss is not usually mentioned; but it is very considerable if the water contains much earthy or metallic sulphates and carbonates, each of which decomposes its equivalent of sodium carbonate. From this cause some works cannot use their well-water or river-water, but must obtain water from a distance through pipes. And of course the water should not contain any acid or acid salt from the condensation of hydrochloric acid or the manufacture of chlorine.

10. The loss by *leakage of liquor* from tanks, pipes, spouts, &c., and by mechanical spilling and the blowing-away of solid products, cannot be considered general, as of course it can be greatly reduced by sufficient care and cleanliness.

Mactear gives the following quantitative results:—

1. Results of seven years' work of a large, well-managed works on the Tyne, decomposing 26,000 tons of salt per annum, but suffering loss through the impurity of the Tyne water:

Obtained as available soda		84·54
Loss as neutral salts	7·26	
„ in process	8·20	
		15·46
		100·00

2. Actual experiment with one furnace:

Available soda		86·93
Loss as neutral salts	5·30	
„ in waste	6·96	
„ mechanically &c.	0·81	
		13·07
		100·00

3. Another actual experiment, most carefully conducted and under favourable circumstances:

Available soda			89·87
Loss as sodium sulphide	2·81		
„ as other neutral salts	1·65		
		4·46	
„ in wash, insoluble	2·20		
„ „ soluble	2·20		
		4·40	
„ in experiment		1·27	
			10·13
			100·00

4. Actual experiment, embracing one year's work:

100 salt yielded 86·318 parts of ash of 48 per cent. available soda			85·91
Loss as neutral salts: sulphate	5·22		
common salt	2·90		
		8·12	
Loss in waste &c.		5·97	
			14·09
			100·00

In these experiments the loss of undecomposed sodium chloride is included, which Mactear estimates at less than 2 per cent.

Cost Accounts.

Gossage ('A History of the Soda Manufacture,' p. 21) states the cost of producing a ton of soda ash, as far as the raw materials are concerned, as follows:—

	£	s.	d.
$1\frac{1}{4}$ ton of Irish pyrites	1	15	0
1 cwt. nitrate of soda	0	12	0
$1\frac{1}{4}$ ton of salt	0	10	0
$1\frac{1}{2}$ ton of limestone	0	10	0
$3\frac{1}{2}$ tons of coals	1	1	0
	£4	8	0

This refers to Lancashire prices in 1861, and is irrespective of wages, repairs, packages, interest on capital, and so forth.

Stevenson and Williamson (Richardson and Watts, Chem. Technol. iii. p. 318) state the cost of a ton of refined alkali of 48 per cent. in 1860 as follows:—

cwt.	qr.	lb.			£	s.	d.		£	s.	d.
6	1	9	sulphur	at	7	17	9	per ton	2	10	7¾
0	2	8	nitrate of soda	„	13	5	2*	„	0	7	7½
23	2	1	salt	„	0	16	3¾	„	0	19	2¼
33	0	10	chalk (with 20 per cent. water)	„	0	1	5½	„	0	2	5¼
67	2	7	coal	„	0	2	11¼	„	0	9	11
Wages									1	10	2
Repairs									0	17	1¼
Interest on capital									0	6	4¼
Expenses of management, rates, taxes, insurance, &c.									0	5	8¼
General stores									0	2	0¾
Casks									0	10	0
Net cost free on board ship in the Tyne									8	1	2¾

* Net cost after allowing for the value of the resulting sulphate.

It will be noticed that the values of sulphur (employed as brimstone) and nitrate of soda were much higher than now; salt has not changed much in price; but chalk, wages, &c. are much higher now.

Chandelon (Monit. scient. 1864, p. 52) gives the following comparative account of the cost (somewhat purposely exaggerated both in an upward and a downward direction) of a ton (1000 kilog.) of 52-per-cent. soda ash for England and Belgium in 1863, on the basis of the cost of sulphate quoted at p. 161:—

a. *Cost in England.*

			francs.	francs.
1500	kilog.	sulphate	at 62 97	94·51
1550	„	limestone	7·75	10·97
2250	„	coals	4·93	11·07
37½	„	coke	13·53	0·42
Wages				13·74
				130·71
Repairs			4·93	
Packages			10·45	
General costs			9·23	
				24·61
				155·32

(A comparison of Chandelon's figures with those of Stevenson and Gossage, valid for the same period, proves the former to be far too low.)

b. *Cost in Belgium.*

		francs.	francs.
1669 kilog. sulphate	at	106·26	177·34
1920 „ limestone		1·60	3·07
4020 „ coal		9·65	38·78
Lighting			1·08
Wages			29·81
			250·08
Repairs		12·31	
General costs		7·72	
Packages		12	
			32·03
			282·11

In another Belgian works 100 kilog. of soda ash, without general costs, repairs, and casks, came to 245·79 francs.

In 1873 the cost, at a medium-sized Tyneside works, of 1000 kilog. of soda ash amounted to:—

	Prices of 1873.						Prices of 1876.					
	£	s.	d.	£	s.	d.	£	s.	d.	£	s.	d.
850 kilog. pyrites (48 p. c.)... at	1	5	0	1	1	3	at 0	18	0	0	15	4
16 „ nitrate	16	0	0*	0	5	1	10	10	0*	0	3	4
1250 „ salt	1	5	0	1	11	3	0	16	0	1	0	0
1750 „ chalk	0	3	6	0	6	2	0	2	6	0	4	4
3000 „ coals and coke	0	12	6†	2	2	0	0	5	6†	0	16	6
Casks				0	13	0				0	11	0
Wages				1	15	0				1	15	0
Repairs				0	15	0				0	12	0
Stores				0	2	0				0	2	0
Management, rates, taxes, insurance				0	6	0				0	6	0
Cost of 1000 kilog. (say 1 ton)				8	16	9				6	5	6

* Price less value of residue.

† Average price, taking in the higher value of coke and mixing-coals *pro ratâ* of their quantity.

The quantity of coals in this account refers to a good quality and somewhat careful work; but in large works, where the supervision cannot be so minute, the consumption is often higher—*e. g.* in one instance on the Tyne, 2932 parts of coals and 310 coke per 1000 ash as it comes from the furnaces, inclusive of offices, loco-

motives, cranes, &c. In badly managed factories and with inferior coal the consumption often rises to five times the yield of ash.

On the basis of the cost of sulphate found at p. 165, the actual cost of 1000 tons of 52-per-cent. hand-made ash in the north of England in the last quarter of 1875 was :—

	£	s.	d.	£	s.	d.
1466 tons sulphate .... at	2	9	0	3591	14	0
1730 „ chalk..............................	0	5	0*	432	10	0
1811 „ firing-coals	0	5	0	452	15	0
733 „ mixing-coals.......................	0	6	0	219	18	0
Wages..				1240	0	0
Repairs				407	10	0
Removal of tank-waste †				137	10	0
Casks and carriage free on board				600	0	0
General expenses ‡......................................				450	0	0
1000 tons of 52-per-cent. ash				7531	17	0
1 ton „				7	10	$6\frac{7}{8}$

* Chalk was then abnormally dear, owing to stormy weather; but its price has been left at the above figure because it more nearly equals the usual price for limestone.

† The waste was sent to sea in hoppers.

‡ Include all selling-commissions and other business expenses &c., but not interest on capital or writing-off on plant.

The following calculation of a French works (in 1878) for 1000 kilog. soda ash of 80–85° Descr. (of which 4° are present in the caustic state) has been obtained by the author :—

	kilog.
Sea-salt	1360
Pyrites, 40–45 per cent.........	1375
Nitrate of soda	40
Limestone	1756·8
Coals	3680·20
Coke	50

CHAPTER XIII.

CAUSTIC SODA.

Sodium forms with oxygen several oxides, of which only Na_2O has any technical importance. It cannot be made directly in the pure state from its elements, but only by combining sodium with the peroxide formed by the burning of sodium in the air. Brought into contact with water it is transformed, with copious evolution of heat, into sodium hydrate (caustic soda). This is a white, opaque, brittle mass of fibrous structure and specific gravity 2·00 to 2·13; it melts below and slowly volatilizes above a red heat. According to Deville, in the melting-heat of cast-iron it splits up into sodium, hydrogen, and oxygen. A hydrate ($2\,NaOH, 7H_2O$) can also be prepared, as we shall see further on. In moist air caustic soda deliquesces, and is afterwards transformed into carbonate. According to Bineau, to dissolve 1 part Na_2O (as $NaOH$) 0·47 part of water is required. According to Osann, 100 parts of water dissolve at

18°	32°	55°	70°	88° C.
60·53	72·91	100·00	116·75	127·02 parts NaOH.

Caustic soda is also readily soluble in alcohol. A solution of soda of specific gravity 1·500 (36 per cent. Na_2O) boils, according to Dalton, at 130° C. The freezing-point of caustic lye is lowered by 0°·509 C. for each gram of the hydrate ($2\,NaO, 3\,H_2O$) per 100 grams water (Rüdorff).

Specific Gravity of Caustic-Soda Solution at 15° C.
(Gerlach, Zeitsch. anal. Chem. viii. p. 279.)

Percentage of the solution.	Of Na_2O.	Of NaOH.	Percentage of the solution.	Of Na_2O.	Of NaOH.
1.	1·015	1·012	31.	1·438	1·343
2.	1·020	1·023	32.	1·450	1·351
3.	1·043	1·035	33.	1·462	1·363
4.	1·058	1·046	34.	1·475	1·374
5.	1·074	1·059	35.	1·488	1·384
6.	1·089	1·070	36.	1·500	1·395
7.	1·104	1·081	37.	1·515	1·405
8.	1·119	1·092	38.	1·530	1·415
9.	1·132	1·103	39.	1·543	1·426
10.	1·145	1·115	40.	1·558	1·437
11.	1·160	1·126	41.	1·570	1·447
12.	1·175	1·137	42.	1·583	1·456
13.	1·190	1·148	43.	1·597	1·468
14.	1·203	1·159	44.	1·610	1·478
15.	1·219	1·170	45.	1·623	1·488
16.	1·233	1·181	46.	1·637	1·499
17.	1·245	1·192	47.	1·650	1·508
18.	1·258	1·202	48.	1·663	1·519
19.	1·270	1·213	49.	1·678	1·529
20.	1·285	1·225	50.	1·690	1·540
21.	1·300	1·236	51.	1·705	1·550
22.	1·315	1·247	52.	1·719	1·560
23.	1·329	1·258	53.	1·730	1·570
24.	1·341	1·269	54.	1·745	1·580
25.	1·355	1.279	55.	1·760	1·591
26.	1·369	1·290	56.	1·770	1·601
27.	1·381	1·300	57.	1·785	1·611
28.	1·395	1·310	58.	1·800	1·622
29.	1·410	1·321	59.	1·815	1·633
30.	1·422	1·332	60.	1·830	1·643

The hydrometer, of course, can only be employed for testing pure liquors; those which contain other salts must be tested alkalimetrically. In the latter case sodium carbonate, silicate, and aluminate are equally reckoned as carbonate, unless they are separately estimated. This is usually done only with carbonate, especially in the case of solid caustic. It is best estimated by dissolving a weighed quantity of caustic, adding barium chloride, filtering, washing the $BaCO_3$ with hot water and exclusion of air, and titrating the precipitate with normal hydrochloric acid.

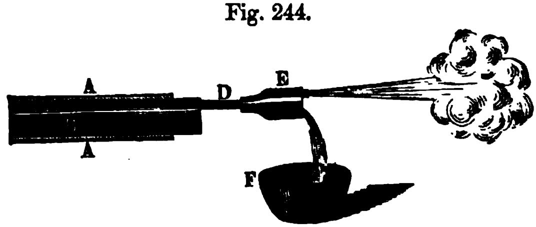
The presence of chloride and sulphate is proved by the ordinary reagents, that of iron also by the colour, that of sulphide &c.

in the same way as in the case of soda ash, to which we must refer the reader.

Chemically pure caustic soda is made from sodium by the Magnesium-Metal Company at Manchester, for analytical purposes (Dingl. Journ. clxxxvi. p. 308). A drop of water is put into a hemispherical silver dish of about 18 litres capacity; a block of sodium is cut into square pieces of 1½ inch side, and one of these laid on the drop of water. The dish, which is cooled on the outside by a stream of cold water, is turned round by hand and shaken so as to offer a large cool surface to the deliquescing sodium and to prevent an explosion. A milky mass is thus produced, to which fresh pieces of sodium and drops of water are gradually added, with constant agitation of the silver dish, till several pounds of the metal have been used. There remains a stiff residue, only covered by a few drops of a milky liquor. It is heated to redness on a gas-furnace till the water is driven off; and the melted sodium hydrate is poured into moulds.

The *sodium* itself is made in Manchester by the process of Deville (Ann. Chim. Phys., Avril 1856), in wrought-iron retorts, protected against the destructive action of many hours' white heat by outer tubes of plumbago; the latter remain in the furnace till they are used up; and as they reach right through its sides, the retorts can be easily exchanged. These are wrought-iron tubes (cast-iron would melt) of 3 feet 6 inches length and 5 inches diameter, closed at the ends by wrought-iron plugs luted with fireclay; one of these contains the tube for conveying the vapour into the receiver. Each retort holds about 30 lb. of the mixture of coal, coke, chalk, and dry sodium carbonate, which are each by itself most finely ground, mixed up, and ground again. Deville's prescription is 30 sodium carbonate, 13 coal, 5 chalk. On heating, first carbon monoxide and hydrocarbons escape and issue from the retort, and afterwards sodium vapours make their appearance. In fig. 244, A is the plumbago jacket, B the wrought-iron retort, D

Fig. 244.



the gas-tube, E the condenser. The latter is flat, like a book, 9 inches long, 5 inches broad, and 1 inch thick. At the end opposite to the furnace it has two slits, one above the other, ⅜ inch wide and 1 inch high, occupying the whole internal width of the vessel. The neck of the retort and the condenser are ground to fit each other, and connected without cement. During the operation a current of gas a yard in length issues from the upper slit and burns; the sodium vapour condenses in the receiver; but the sodium remains in the liquid state and runs off in drops into the vessel F, filled with a hydrocarbon which ignites only at a high temperature. Lastly, the distilled sodium is fused under oil, and poured into square blocks; it is sold at 5*s.* per lb. (At Salindres from 9 kil. sodium carbonate 1 kil. of sodium is obtained, which costs 11·32 francs per kilog.). The operation lasts six or eight hours, and requires a full white heat. Each furnace contains three retorts, and is attended by one man and three boys; the latter have especially to take care that the receivers do not get stopped up, by cleaning them through the slits with red-hot iron wires. In spite of this the receivers have to be frequently exchanged, sometimes after only 20 minutes, in order to be cleaned. For this purpose they are dipped into water, the side plates are unscrewed, cleaned, and put together again. In this way 4 or 5 cwt. of sodium per week is made; and this is employed in chemical laboratories for preparing pure caustic, and for manufacturing magnesinm, aluminium, and sodium amalgam (for the extraction of gold).

Caustic Soda.

By this name (or "caustic" only) is understood a commercial product consisting entirely or principally of sodium hydrate. There is also a trade in *caustic liquor,* which is sent out in carboys and is of very varying strength; but, for easily intelligible reasons, this article could never have an extended sale; the cost of packing and carriage even for short distances raises its price so much that consumers nearly always prefer preparing it for themselves from soda ash and lime. This is done by soap-makers, bleachers, paper-makers, and other consumers of caustic liquor. We have the less need to enter into a description of the manufacture of caustic liquor as a commercial product, as it is the first stage in the manufacture of solid caustic, to which we now pass.

The manufacture of caustic from red liquors by means of lead sulphate at Dieuze has been mentioned on p. 489. In the Chapter treating of the various proposals for manufacturing soda we have, for the sake of connexion, enumerated also all those referring to a direct preparation of caustic soda otherwise than by causticizing sodium carbonate with lime; and to that Chapter (the third) we refer the reader.

The manufacture of solid caustic, originally introduced by a German of the name of Weissenfeld, has been entirely developed in England. It is usually stated (according to Hofmann's Report of 1862, p. 27) that the origin of the process now employed dates from 1851; but already on February 20th, 1845, George Brown, one of the partners in Messrs. Tennants & Co., took out a patent in which it is stated that the solution of black ash is to be concentrated till four fifths of the salt are precipitated, and then allowed to stand for some time, till the red liquor is drained off; this is to be boiled down to the consistency of tar; a sufficient quantity of sodium nitrate is to be added, and heat applied till the remaining water has been driven off and the mass has been brought into igneous fusion. Mactear (Report, p. 29) has shown that this was not the invention of Brown, but of Weissenfeld, who, in 1844, fused red liquors with nitre and made perfectly white caustic from it. The manufacture was at that time discontinued because there was no demand for this article; and it seems to have fallen into oblivion. It is just possible that solid caustic was made somewhere between 1845 and 1851; but the fact that not a single English patent about it was taken out during that time tells against that assumption.

Thus much is certain, that, if not the commencement, at any rate a new epoch in the manufacture of solid caustic dates from Gossage's patent of May 18th, 1853. This patent, which also treats of the oxidation of tank-liquor by air in a coke-tower, of the removal of sodium ferrocyanide by crystallization, and of the evaporation of the liquors by running down in a tower provided with horizontal shelves, further speaks of the production of caustic soda from tank-liquor by concentration and without the employment of lime. The liquor, freed from iron sulphide by oxidation by means of air, is gradually treated with a solution of bleaching-powder in order to convert the hyposulphite into sulphite or sulphate, and is concentrated till nearly all the sodium carbonate

and ferrocyanide have been separated as salts. The remaining solution is further concentrated in order to obtain solid caustic.

From that time the general attention of Gossage's neighbours in South Lancashire (which up to this time has remained the principal seat of this manufacture) was directed to this article, which was especially welcome to soap- and paper-makers; and soon caustic soda appeared in trade, but always in a coloured state—blue, green, yellow, red, &c. In 1855 (Nov. 27th) Stott obtained a patent for clearing the liquor of sulphide by means of the oxides of manganese, iron, or zinc; in 1857 (Feb. 21st) another patent of Gossage's and soon many others followed. A very important step was the patent taken out in 1857 (Sept. 23rd) by Bakewell (for Thompson), which introduced the now generally practised mode of packing caustic in sheet-iron drums. Formerly it was poured out onto metal plates, broken up after solidification, and packed in casks (patented subsequently again by Ralston in 1860!)—a very disagreeable kind of work, during which the caustic again attracted much moisture and carbonic acid. Some manufacturers on this account filled up the casks, packed with caustic in pieces, with fused caustic.

As about that time the demand for caustic soda already exceeded the supply, a commencement was made of working up the tank-liquor itself, by causticizing it with lime, whilst previously only red liquors had been used. Still even then "cream" caustic only was made from tank-liquor. In 1858 (Nov. 13th) Messrs. Thomas patented the process now mostly used, viz. causticizing by lime and oxidizing by air in one operation. In 1859 (Feb. 24th) Dale patented the concentration of dilute caustic liquors in steam-boilers &c. for the purpose of usefully applying the steam generated. One of the most important patents was Ralston's (Nov. 22, 1860). He obtained for the first time *white* caustic soda, by raising the heat in the last stage of the process till the iron separated as oxide at the bottom of the vessel, the clear alkali remaining at the top. Previously white caustic or stronger than 60-per-cent. caustic had only exceptionally been made, because at that time the melting-pots were cast too thin and of too uncertain a quality to stand the igneous fusion of caustic long enough for the ferric oxide (and, according to Pauli, crystalline aluminium silicate) to be deposited. Deacon, however, mentions (Chem. News, xxxiii. p. 160) that on August 7th, 1857, he had begun making caustic according to Gos-

sage's patent, and that already on September 17th he had made a batch of white caustic precisely by the process subsequently patented by Ralston; Gamble had perhaps done it even before him. At all events, in 1859, likewise previous to Ralston's patent, Mac Bryde had made white caustic in exactly the same way. For all that, some time elapsed before white caustic became a commercial product. In 1862 it was exhibited in London by Deacon, and by Pauli at Manchester; but it was still a great rarity till the process now used was published by Pauli (Chem. News, v. p. 351; June 28th, 1862). This process has been described minutely by Norman Tate in the 5th, by Morrison in the 31st, and by Davis in the 32nd volume of the 'Chemical News;' and their publications are very amply drawn upon in the following.

A patent of Deacon's (April 10th, 1862), intended to introduce crystallized caustic, has had to be abandoned again. The last important step, the complete or nearly complete substitution for nitrate of soda of air blown into the mass whilst in igneous fusion (not merely into the dilute liquor in a previous stage) was already contained in Ralston's patent of Nov. 22nd, 1860, and in 1865 carried out by Hart (Chem. News, xxvii. p. 207); it was re-invented and patented by Helbig (July 5th, 1870).

Outside of Lancashire the manufacture of caustic could not for a long time be firmly established. On the Tyne since 1864 some caustic had been made; but (excepting a small works, discontinued long ago) it was done by dissolving and causticizing soda ash, which costly process can only exceptionally compete with the Lancashire works. Only for a few years past has white caustic been made from tank-liquors both on the Tyne and at Glasgow, and not in any very large quantity, if compared with Lancashire, where one single factory at Widnes, when in full swing, turns out 250 tons, several others in the same place and four or five at St. Helens from 60 to 80 tons, of 60-per-cent. caustic per week. All the white caustic is there made by causticizing tank-liquor with lime, the cream caustic mostly from red liquors without lime. From the latter by very special care white caustic can also be made; but this rarely pays, and is only done at a few works.

In Germany caustic has been made ever since 1859; but at first it was of very inferior quality; recently this branch of alkali-making has extended greatly there in consequence of the demand made upon it by the manufacturers of alizarine, of wood-pulp, &c.

There is now a comparatively large quantity of caustic soda of the best quality and highest strength made both in Germany and Austria (Aussig). In France this manufacture is not yet by any means very extensive.

Already in making the *black-ash mixture* regard must be had to the caustic intended to be made from it. Davis (Chem. News, xxxii. p. 165) states the following as mixtures actually employed in different works :—

	I.	II.	III.	IV.	V.
	cwt.	cwt.	cwt.	cwt.	cwt.
Sulphate of soda	2·5	3	2·5	2·5	—
Limestone	2·75	3	1·5	—	3
Lime mud from causticizing	—	—	2·5	5	—
Coal	1·5	1·625 to 1·75	1·5	1·5	1·5
Fished salts (see below)	—	—	14 lb.	—	2

The mixtures IV. and V. ought only to be employed quite exceptionally, and doubtless do not yield very good black ash; the 2 cwt. fished salts only contain about 0·7 cwt. real sulphate. Of the smaller balls 25 to 33, of the larger ones usually 25 are made in 24 hours, with two shifts of men.

Gossage once proposed a mixture of 3 cwt. sulphate, 3 chalk, and 3 coal for this purpose; but this has not turned out well.

We shall now pass on to the *manufacture of white caustic from tank-liquor by means of lime,* and commence with the

Causticizing.

We have seen before that formerly in some places soda ash was dissolved for caustic, and that in apparatus precisely similar to those employed in manufacturing soda crystals. This plan is still employed at paper-mills &c., where caustic liquor is made for home use; but where caustic is made for the trade, the same plan is very seldom followed now, because it is too expensive; the *tank-liquor* obtained on lixiviating black ash is usually treated with lime.

This in Lancashire is generally done in horizontal semicylindrical vessels, frequently old boilers cut in halves, 20 to 30 feet long, and 6 to 7 feet wide and deep. They are always provided with a feed-pipe for tank-liquor, a water-pipe, a steam-pipe, and a run-off cock; but the way in which the agitation of the liquor is produced varies much. In some cases no mechanical contrivance whatever is em-

ployed for this purpose; the lime is put, in an unslaked state, into a cage of iron rods constructed on one side of the vessel, and slakes there in the liquor itself—the coarser parts, such as stones &c. being retained in the cage, while the finer cream passes through. The steam-pipes end in different parts of the vessel perpendicularly close above the bottom; so that the steam bubbling up itself causes a good agitation of the liquid. Such apparatus are only adapted for a comparatively small scale of working, and do not utilize the lime to the full extent possible. Hence usually either mechanical agitators (mostly driven by a donkey-engine bolted to the vessel itself), or air-injectors (of which Koerting's is the best shape) are provided. The current of air injected, and finely divided by branch pipes or a perforated false bottom, not merely produces a very good agitation of the lime mud with the liquid, but also acts at the same time as an oxidizing agent upon the sodium sulphide and ferro-sodium sulphate, thus dispensing with the previous application of Gossage's or Hargreaves's apparatus (p. 517), which formerly were a good deal employed for caustic.

A peculiar causticizing apparatus is employed at Aussig. In the centre of a cylindrical vessel, provided with a perforated false bottom a little above the true bottom, there is a vertical tube, open at both ends, reaching below the false bottom and ending about 12 inches below the top of the vessel. In its centre revolves a shaft, driven from above, carrying blades in the form of an Archimedian screw and constituting an inverted turbine, by which liquid is continuously raised from underneath the false bottom, poured over the edge of the central tube, filtered downwards through the lime, and so forth. This arrangement answers especially well for washing the lime mud; with it a sticking fast of the agitator, which easily happens with thick lime mud, cannot occur.

In other places there are perpendicular shafts with horizontal arms, from the lowest of which chains hang down and drag iron balls behind them on the bottom of the vessels and thus keep it clear of sediment.

The opinions of practical men vary on the point whether causticizing by mechanical agitation or by injection of air is to be preferred. So much is certain, that the injector requires more steam than a mechanical agitator; but in favour of the former are the simplicity of the apparatus and the fact that the sodium sulphide is oxidized at least as far as hyposulphite, and the iron is mostly

precipitated. In England this way of causticizing (by injection of air) is now almost exclusively practised.

The tank-liquor should be quite as well settled as for soda ash; at the first glance this would not seem to be necessary, as one would think that the lime mud would clear the liquor; but that is not the case, and bad settling is revenged by a bad quality of caustic. The lime should be of good quality, since inferior (clayey) lime yields badly settling liquors.

The tank-liquor is always diluted with water or the washings from the lime mud of former operations, to 16° or 20° Tw. It is well known that concentrated solutions cannot be completely causticized; but up to 20° Tw. there is no danger, and there is then less water to be evaporated than at the lower strength. In some works even the strength of 23° Tw. is employed; and then the liquors are not completely causticized, only about 92 per cent. of the carbonate; coals for evaporation, however, are saved. According to Parnell's patent of Nov. 7, 1877, soda-liquors up to 40° Tw. can be causticized by lime if a higher pressure and temperature are applied—that is, in closed vessels provided with agitators. The pressure must be kept up till the caustic liquor has been separated from the calcium carbonate, because otherwise an inversion of the reaction would take place. An additional patent of Parnell and Simpson's (of June 1st, 1878) contains several improvements in the details of the apparatus and process.

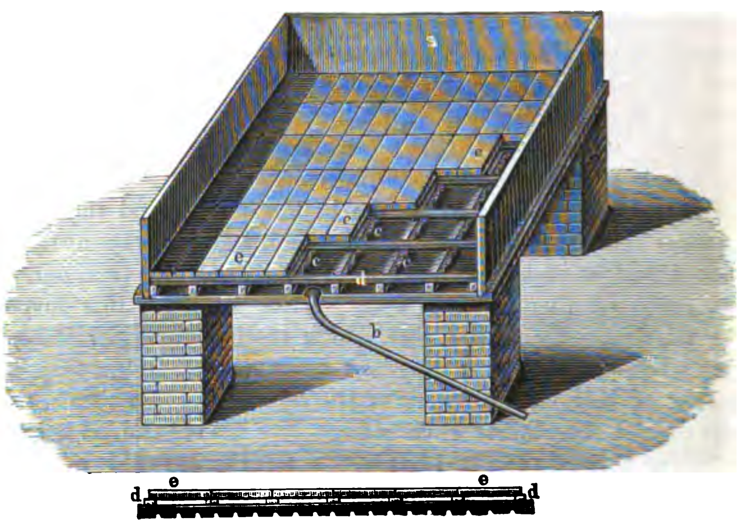
The mixture is brought to the boiling-point; and then, with constant agitation of the liquid, the lime is added, always unslaked, since it will be slaked as soon as it gets into the liquid, and the heat given off thereby saves some steam. It is for this purpose that the iron cage is provided, which receives the quicklime and retains the stones &c. A practised workman can judge, from the manner of boiling, the colour of the liquor, and other tests, with some degree of certainty when enough lime has been added to make the liquor perfectly caustic; but besides this there are always special tests, made by filtering a sample and adding a little hydrochloric or sulphuric acid, which ought not to produce any effervescence. Now either the whole batch can be run off into a special settler, or it is allowed to settle in the operation-pan itself (as it is called in Lancashire), for which only half an hour is required; then the clear liquor is gradually drawn off by means of a swivel-pipe (figs. 237 & 238 on p. 558), and pumped by means of a centrifugal

pump (unless there is a natural fall) into the liquor-settler, where it must remain perfectly quiet. Mostly a second operation is performed in the pan without removing the lime-mud: more tank-liquor and water is run in, the temperature raised to boiling, the liquor causticized (for which not quite so much lime is required as the first time, because a little remained behind in the mud from the first operation), and again the clear liquor run off. More rarely the whole contents of the operation-pan are run onto the filter, where the lime remains behind.

The lime mud is now mixed with a little fresh water, brought to a thin state by the agitator, and either allowed to settle once more so that the dilute liquor can be drawn off, or at once brought upon the filter.

The *filters* employed are of a peculiar construction, originated by Ralston, Gossage, and Shanks. Fig. 245 shows their ordinary shape. A low trough, *a*, made of stone flags, or more usually an iron tank

Fig. 245.



of about 20 × 10 feet length and width and 4 feet depth, or one half of a steam-boiler cut in two the long way, is placed a little above the ground-level, and its bottom inclined a little towards one side, from which the pipe *b* takes away the liquor. On its bottom there are a number of nicked laths *c c*, the nicks allowing the liquor to

circulate; on these lie the bearers *d* for the porous flags *e e*, joined with cement, so that the liquor must pass through the pores of the flags. More usually bricks on edge are placed on the bottom of the filter, about 2 inches apart; in the centre a wider channel is left and covered over with bricks or flags. The whole is covered with an 8-inch layer of coke or (less suitably) limestone in pieces, upon this a second layer of smaller, and a thin layer of very small pieces; last of all comes a layer of pure coarse sand or small coal, and on the top of this cast-iron or wrought-iron grids, upon which the men can work with the spade. Before use the grids are covered with furnace-cinders or small coal. In a filter of 4 feet depth there must be thus a space of 18 inches or 2 feet depth left for the lime mud. Shanks places strong iron bearers 12 inches above the bottom, on the top of these perforated metal plates, then a wire gauze of 4 holes per linear inch, then strong, loosely woven calico, and on this another wire gauze. Before filtering, stiff lime mud is plastered round the corners of the filter, in order to prevent the entrance of air in these places on evacuating the filter.

Sometimes the pipe *b* is simply conveyed into the weak-liquor well; but it is much better and more usual to assist the filtration by a vacuum. For this purpose the pipe *b* enters a small air-tight iron boiler of 120 to 200 cubic feet capacity, which is very suitably placed above the operation-pan; this is connected with the air-pump, and is provided with an air-cock, a run-off cock in the bottom, and a water-gauge. Or else the vacuum is produced by injecting and subsequently condensing steam in a separate boiler.

As soon as the dilute lime mud has run upon the filter, the air-pump is set in motion, and first the air and then, as it collects, the liquid from underneath the filtering-bed are removed. Cracks are very soon formed on the surface of the mud—which must at once be closed by means of a rake, running at the same time a jet of water onto the mud and working it well through with it, so as to wash out the caustic contained in it. At Aussig the formation of cracks and the disturbance of the vacuum are much more completely and certainly prevented by means of a perpendicular shaft with slanting side arms, continuously turning up and laying down the surface of the mud on the (cylindrical) filters. After three or four hours the paste has become stiff and no more liquor runs out. The vacuum-pump is now stopped; and the collected washings are employed for the next causticizing operation. Some do not

wash the lime mud at all, since it is again worked up in the black-ash furnace, and its soda is thus utilized. But as in any case water is required for diluting the liquor previously to causticizing, washing in the filter seems preferable.

The composition of washed lime mud is shown in the following analyses by Davis (*loc. cit.* p. 187):—

	A.	B.
Calcium hydrate	2·825	2·652
Sodium hydrate	1·906	1·663
Sodium chloride and sulphate	0·244	0·206
Calcium carbonate	40·170	42·031
Calcium hydrate	3·756	3·072
Silica	0·673	0·774
Alumina	0·255	0·324
Iron peroxide	0·048	0·708
Magnesia	0·086	0·095
Soda	1·832	1·600
Water	47·986	46·577
	99·781	99·702

The first three components, bracketed, were soluble when 5 grams of the mud were digested in 100 cub. centims. water at 100° C.

According to Kynaston, lime mud retains as much as 5 or 6 per cent., according to Norman Tate's experiments on the small scale 2·5 or 3 per cent. Na_2O. Since, with good lime, for a ton of 60-per-cent. caustic 11 cwt. of lime are reckoned, which yield about 36 cwt. of mud, a percentage of 2·5 Na_2O in the dry or 1·25 in the wet state will cause a loss of 50 lb. of soda per ton of caustic soda. With inferior lime, of which 1 ton is required, 3 tons of mud are obtained, and consequently there is a loss of ¾ cwt. of Na_2O per ton of caustic.

This lime mud is generally employed for replacing a portion of the limestone in a fresh black-ash mixture, and is all the more adapted for this as it is in a finely divided form, and as the soda still present in it in a soluble form, but not completely washed out, is in this way utilized. It is possible to use a good deal of it, as the mixtures given on p. 595 prove; and it is employed in the damp state, because drying would be too troublesome.

Where this certainly most rational way of utilizing the lime mud

cannot be followed, *e.g.* in soap-works where they buy soda ash and causticize it, it has often been attempted (as proposed by Muspratt) to dry the mud and reconvert it into caustic lime in order to employ this over again for causticizing soda. This, however, has always failed—partly because the lime thus made was dearer than fresh lime, and partly because in drying it fell to powder and could not be properly burnt.

A locally restricted utilization of the lime mud has been carried out by Nackh and Co. at Vienna (Wagner's Jahresb. 1872, p. 257): they employ a part of it for making carbonic acid for mineral waters, and mix the calcium sulphate thus obtained in different proportions with another portion of the lime mud, subject the mixture to strong pressure, and mould it into pieces for writing-chalk.

Davis gives the following analyses of dilute tank-liquors:—A, before causticizing; B, the same after causticizing, the agitation having been produced by *injection of air*.

	A. grams.	B. grams.
Iron sulphide	traces	——
Ferric oxide	——	traces
Sodium sulphide	1·068	none
„ sulphite	0·151	0·264
„ hyposulphite	1·137	1·864
„ sulphate	5·423	5·006
„ chloride	8·576	7·995
„ silicate	0·852	0·176
„ aluminate	2·490	1·438
„ carbonate	53·167	2·954
„ hydrate	44·280	74·000
„ ferrocyanide	0·093	0·086
„ sulphocyanide	0·054	0·050
„ phosphate	traces	traces
Insoluble	0·849	none
Total solids per litre	118·140	93·833
Spec. gravity at 13° C.	1·100	1·090

The next sample had been made from more *dilute* tank-liquor (of 15° Tw.) and by *mechanical agitation*; it showed at 11° C. spec. gravity 13° Tw.

	grams.
Iron sulphide	traces
Sodium sulphide	1·092
„ hyposulphite	1·264
„ sulphite	trace
„ sulphate	3·264
„ chloride	4·212
„ silicate	0·151
„ aluminate	0·584
„ carbonate	7·844
„ hydrate	50·400
Other constituents	0·200
Total solids per litre	69·011

This shows that by agitating with injected air, unlike mechanical agitation, the sodium sulphide is almost completely destroyed and principally converted into hyposulphite, according to the equation

$$2Na_2S + 4O + H_2O = Na_2S_2O_3 + 2NaOH.$$

On continued blowing, probably the hyposulphite would be transformed into sulphate; but there is no time for it in this process.

It can further be seen from the above analyses that most of the silica (up to 80 per cent.) is removed in causticizing. Also 42 per cent. of the sodium aluminate have been removed as an insoluble calcium aluminate; the aluminate proceeds partly from the tank-liquor, partly from the "caustic bottoms," which are dissolved in water to 20° or 30° Tw. and causticized along with tank-liquor.

We have seen in a former chapter (p. 489) that several metallic oxides have been proposed for removing the sodium sulphide from the liquor, as iron, zinc, and manganese oxides; the metallic sulphides produced were to be washed, dissolved in hydrochloric acid, and the hydroxide recovered by precipitation with milk of lime. This plan has been abandoned after many endeavours; even zinc oxide, which promised best, was not applicable, because zinc sulphide is a slimy precipitate which will not settle in an alkaline liquor. Lead oxide only has been, as litharge, employed successfully in two works; but on account of its cost, and as its recovery is practically impossible, it is only employed for (nominally) 76-per-cent. caustic (containing nominally 98 per cent., in reality 95 or 96 per cent. NaOH). This is the article sold by the Greenbank

Chemical Company at St. Helens, which fetches a much higher price than ordinary caustic, but naturally only commands a restricted sale. The litharge is added in causticizing; it amounts to less than 50 lb. per ton of 60-per-cent. caustic, and reduces the consumption of nitre to less than 6 lb. per ton. The litharge being very heavy renders it necessary to agitate very energetically, and that mechanically, since by the application of air sulphite is formed from the sulphide instead of caustic, and thus the advantage procured by the lead oxide is lost. Probably the best way of using it would be to dissolve it in strong caustic liquor of 50° Tw. The lead sulphide remains mixed with the lime mud and is lost, but does not interfere with its use in the black-ash mixing.

The Concentration of the Liquor.

The caustic liquor is now finished; but it is diluted, viz. from 13° to at most 20° Tw., and its concentration is accordingly a very important task, in which the economy of fuel is the principal object. Parnell's process (p. 597) would save some fuel; but it is questionable whether this is equivalent to its extra cost.

The process patented by Dale would seem the most rational, according to which the first concentration of the liquor takes place in a steam-boiler, and the steam generated is utilized as such. This can be done for driving an engine or for heating-purposes, or for concentrating a fresh quantity of liquor at a lower pressure. At most of the few works where this process was employed the steam was used in causticizing tank-liquor; once the author found it employed (in a small factory) for supplying the vitriol-chambers. The concentration of caustic liquor in steam-boilers has the disadvantage that at a certain stage the liquor has a tendency to froth over. This is avoided by placing within the boiler, over its hottest place, a cast-iron funnel with its mouth downwards, touching the shell of the boiler only in a few places; the most ample formation of bubbles and froth takes place underneath the funnel; and the rising froth, owing to the shape of the funnel, must carry some liquor along, which constantly runs over at the top, flows back upon the boiling and frothing liquid, and thus abates the violence of the frothing.

According to Hofmann's Report (1862), p. 27, liquor might be concentrated up to spec. gravity 1·24 or 1·25 without the slightest

inconvenience in steam-boilers; the author has met with this in actual practice only once, though in several instances the strength has been 1·20; but, according to Davis, in no case ought a spec. gravity of 1·15 to be exceeded. But this process appears to have been abandoned everywhere, because the boilers are much acted upon by the sodium sulphide, and because with the slightest carelessness of the attendants very awkward consequences occur. In any case, if the liquor is concentrated in steam-boilers, the causticizing ought to be effected by injection of air, or the liquors desulphurized with the assistance of litharge; nor ought the point ever to be attained at which any salts may be precipitated.

The proper concentration, in England, always takes place in *boat pans*, which are partly heated by the waste fire of the black-ash furnaces, partly, as this is not sufficient for caustic liquors, by special fires. They are either of cast iron or of wrought iron; their construction and setting have been described in detail on p. 502 *seq*. In some works there are two cast-iron pans, in others two wrought-iron pans, placed behind the black-ash furnaces, one behind the other; in others there is first a cast-iron, then a wrought-iron pan. The pan placed next to the furnace is so arranged that its bottom is on a level with the furnace-arch; the following one is placed about 6 inches higher. The dilute liquor is run into this pan first, and further concentrated in the first pan. Some works, less rationally, feed the pan next to the furnace with weak liquor. The back pan (mostly of wrought iron) can hardly get the liquor up to boiling and concentrate it up to 28° Tw.; in the front pan (often of cast-iron) the liquor gets up to 50° Tw., and is then run off by a 2-inch pipe and cock into the separately fired "strong"-pans. Sometimes these cast-iron pans are heated by the black-ash-furnace fire; one gets the liquor up to 24°, the middle one to 54°, and the last one to 70° Tw.; at this strength salts begin to separate. A decidedly wrong arrangement is that of fixing a wrought-iron pan over the black-ash furnace in the place of an arch, and a second one behind it; the slight gain in evaporating-power cannot make up for the continual stoppages and repairs.

The German works, even for this object, do not apply any boat-pans, but flat-bottomed pans, both because they shun the more difficult constructions and repairs of the former, and because, as they contend, they have purer liquors, and hence less salts, than the English works.

The "strong"-pans, heated by a separate fire, are also either of cast or wrought iron; in the former case they are always fired in sets of two or three, in the latter, where they are made sometimes 30 feet long, singly. As the first strong-pans boil very vehemently, they are provided with 9-inch sheet-iron borders, attached to the flanges of the pan by several pieces riveted on.

In any case all the pans, beginning from the caustic-liquor settlers, must be arranged so that the liquors can run spontaneously from one pan to the other. Pumping is excluded for the more highly concentrated stages; and if such a liquor has to be transferred to a higher level, the costly and disagreeable operation of baling by hand must be resorted to, which in the last stage, that of finishing, is not avoidable. If it were altogether indispensable, no doubt mechanical contrivances could be applied to this; but it is certainly simpler to lay out the plans from the first so as to do away with such things —that is, to place the liquor to settle at a sufficient elevation.

The boiling is always continued up to certain degrees of concentration; and, as usual, these are ascertained by the hydrometer. But as this does not give quite uniform results for the higher strengths, and is not always very easily applicable, the thermometer is employed as well, since the boiling-point of the liquors regularly increases with its concentration.

When these have attained the point at which the hydrometer indicates 70° to 72° Tw., and the thermometer 138° C., the fire is drawn out or allowed to burn down, and the contents of the pan are allowed from half an hour to two hours to settle, so as to get clear and to deposit salts. If 70-per-cent. caustic has to be made, the English works concentrate further, up to 80° or 85° Tw., as will be described further on. After settling, the clear liquor is run off by a swivel-siphon, and the remaining salt put into drainers with false bottoms by means of a perforated shovel, whence, after thorough draining, it is taken back to the black-ash furnaces. In other cases the salts are fished out during the evaporation in the weak-pans, and are consequently less caustic. Frequently the salt is left in the pan and partly-concentrated liquor is run upon it; it is then fished out, after having been washed to some extent in this way. The salt obtained by fishing from strong liquors consists mainly of monohydrated sodium carbonate and anhydrous sodium sulphate (A); that fished from weaker liquors, of hydrated salts (B). Davis's analyses are :—

	A.	B.
Insoluble	0·384	0·214
Sodium sulphite	2·734	0·793
„ hydrosulphite	0·316	0·252
„ sulphate	29·583	24·499
„ chloride	3·978	1·872
„ silicate	traces	traces
„ aluminate	traces	traces
„ carbonate	27·984	22·684
„ hydrate	15·360	7·680
Water (by diff.)	19·661	42·006
	100·000	100·000

Morrison states the composition of fished salts as follows :—

Water	18·00
Na_2CO_3	39·00
NaOH	9·00
Na_2SO_4	29·00
NaCl	0·50

Besides there was some hyposulphite and sulphite (evidently this analysis, like all others in Morrison's paper, is only a rough one). The total amount of "salts," all of which must pass through the black-ash furnace again, with moderately good liquors does not exceed 20 to 25 per cent. of the weight of the finished caustic.

Already in boiling down care must be taken lest the above salts adhere to the pan-sides, a task which is very much facilitated by the shape and the manner of setting the pans.

Quite differently composed is that portion of the salts which is deposited in the settlers, of course whilst the liquor is cooling; here sodium chloride predominates, as is shown by the following analyses of Davis:—

	A.	B.
Insoluble (chiefly FeS)	1·143	0·867
Sodium sulphide	traces	0·077
„ sulphite	2·734	1·013
„ hyposulphite	0·316	0·146
„ sulphate	9·768	5·772
„ chloride	37·674	60·443
„ silicate	traces	traces
„ aluminate	traces	traces
„ carbonate	15·052	5·683
„ hydrate	13·440	10·773
Water (by diff.)	19·873	15·226
	100·000	100·000

This salt is not deposited in very large quantities; so that it need only be cleared out once every fortnight. It is of a greasy nature, cannot be easily separated from its mother liquor, and is evidently nothing like so well adapted for black-ash making as the former salts. In some works it is not separated at all, but always at the expense of the quality of the caustic; in this case the liquor must be allowed to settle much longer in the pans themselves, say six or eight hours.

The strong-pans are run off about once every 24 or 30 hours; and five of them are required to make up a 10-ton finishing-pot. Already in the pans themselves a little nitrate of soda is added, when about the spec. gravity 60° Tw. has been reached. The men assume that this precipitates the salts better, and keeps the pans free from incrustations. Of course any sodium sulphide present is thus oxidized. An excess of nitre at this stage would mean a loss, as it would be precipitated along with the salts. If the liquor has been oxidized by air in causticizing, no nitre whatever need be added, even if the liquor is reddish and contains traces of sulphide.

According to Pauli, at this stage, so long as the boiling-point of the liquor does not exceed 138° to 143° C., the sodium sulphide is quietly oxidized into sulphate, nitrite being formed; at 155° C. ammonia is first given off in quantity, with lively effervescence; when the boiling-point exceeds 155° C., the evolution of ammonia ceases again and a tempestuous evolution of nitrogen sets in. A

portion of the ammonia is also furnished by the decomposition of the cyanides. Pauli's equations are :—

1. $Na_2S+4NaNO_3=Na_2SO_4+4NaNO_2$;
2. $Na_2S+NaNO_3+2H_2O=Na_2SO_4+NaOH+NH_3$;
3. $5Na_2S+8NaNO_3+4H_2O=8NaOH+5Na_2SO_4+8N$.

Muspratt, by introducing hyposulphite and sulphite, arrives at the following equations :—

1. $2Na_2S+Na_2S_2O_3+2NaNO_3+3H_2O=4Na_2SO_3+2NH_3$;
2. $Na_2S+Na_2S_2O_3+Na_2SO_3+2NaNO_3+3H_2O=4Na_2SO_4+2NH_3$.

Muspratt's equations are far too specialized for such a complicated process, and hence contribute little to explain it; moreover the second one is wrong, as it exhibits one atom of oxygen less on the left side than on the right side. (The original, in the old notation, puts it: $NaS+NaO,\ S_2O_2+NaO,\ SO_2+NaO,\ NO_5+4HO=4NaO,\ SO_3+NH_4O$.)

In contradiction to Pauli, Davis asserts that even below 138° C. NH_3 is given off and but little "sulphite" is formed (this is probably a clerical error for *nitrite*). He represents the four stages of oxidation thus :—

1. $2Na_2S+NaNO_3+3H_2O=Na_2S_2O_3+3NaOH+NH_3$;
2. $2Na_2S_2O_3+3NaOH+NaNO_3=4Na_2SO_3+NH_3$;
3. $5Na_2SO_3+2NaNO_3+H_2O=5Na_2SO_4+2NaOH+N_2$.

The first reaction takes place below 138° C.; and the hyposulphite formed remains mostly dissolved in the liquor. The second reaction sets in a little above or below 152° C.; the resulting sodium sulphite rises and floats on the top of the pots as a white scum. When the last reaction commences it would be difficult to say; but in most cases the evolution of ammonia stops at 182° C. and nitrogen takes its place. All these reactions cannot occur unless an excess of nitre has been added, consequently not at the stage already described, but later on in the finishing-pots. But even without the addition of nitre sulphite is formed at a temperature of about 160° C., probably by the action of the air upon the hyposulphite, thus :

$$Na_2S_2O_3+2NaOH+O_2=2Na_2SO_3+H_2O.$$

Another portion of the hyposulphite is decomposed at a higher temperature, especially in contact with the heated pans, in the following way:

$$Na_2S_2O_3 + 2NaOH = Na_2SO_4 + Na_2S + H_2O.$$

Sodium sulphide itself is oxidized by the action of the air; and in cases where the liquors had been completely oxidized during causticizing, some pots have been finished without a particle of nitre going into the liquor at any stage. This observation of Davis's agrees with the author's observations at Aussig (see below).

In any case, when nitrate is added to liquors not yet arrived at the 138° C. boiling-point, ammonia is given off and principally hyposulphite is formed, which remains dissolved, except a small quantity of sulphite which falls down with the salts and may be seen in the preceding analysis. If nitrate of soda is then added to the pans, it ought to be in the proportion indicated by Davis's first equation—that is, only one $NaNO_3$ for $2Na_2S$, whilst Pauli's first equation requires eight times as much. Davis found that when nitrate of soda was added in the proportion indicated by his theory and then boiled to 138°, 90 per cent. of the sulphide was oxidized, while a very small proportion only should have been so if nitrite and sulphate had been formed.

Also the reaction taking place during the igneous fusion of the mass is explained by Davis in his third equation differently from Pauli, because at this stage no other water can be present than that chemically combined with sodium oxide.

There is also *another method of concentrating*, beside that described above. In this the liquor is only boiled down to 50° Tw., of course entirely in boat pans by the waste heat of the ball-furnaces; no salts are separated, or but an insignificant quantity; and the liquor, without any settling, is run into caustic-pots, where it is boiled to 138° C., when the fire is drawn and the contents of the pots are allowed to settle. The sulphide, carbonate, and chloride, with several other salts, are deposited here in one operation and the supernatant liquor baled off, to be treated as described below. Weak liquor is then run upon the deposited salts, which are fished out, drained, and sent into the black-ash mixing. Their composition, according to Davis, is as follows:—

	A.	B.
Insoluble matter (chiefly FeS)...	0·742	1·004
Sodium sulphide	0·116	0·097
„ hyposulphite..............	0·274	0·718
„ sulphite.....................	8·723	2·695
„ chloride....................	7·024	5·834
„ sulphate....................	22·773	26·432
„ silicate	traces	traces
„ aluminate	traces	traces
„ carbonate	21·559	24·218
„ hydrate	8·417	10·116
Water (by diff.)......................	35·372	28·886
	100·000	100·000

Of these two methods the first (boiling down in boat pans, partly by separate fires, up to 138° C., salting out by settling in the pans and settlers and then only conveying to the pots) causes more labour and repairs than the second (boiling down in boat pans only up to 50° Tw., then further in the pots and separating all salts in one operation); this latter, however, causes greater expense for fuel, about as much as the labour and repairs amount to in the former case; so that it is an open question which is the best process to adopt.

Davis gives the following analyses of strong liquors as they run into the pots :—

	A. grams.	B. grams.
Iron sulphide....................	0·740	none
„ peroxide....................	none	0·071
Sodium bisulphide...............	0·462	none
„ sulphide..................	0·531	none
„ sulphite..................	none	none
„ hyposulphite............	12·324	19·908
„ sulphate	2·964	0·120
„ chloride..................	19·890	26·325
„ silicate	1·758	1·555
„ aluminate	6·984	5·784
„ carbonate	25·840	22·506
„ hydrate	552·000	560·000
„ sulphocyanide	0·342	1·240
Total solids per litre......	623·835	637·509

A was from liquor thoroughly oxidized in causticizing, boiled down to 138° C.; it was 93° Tw. at 11° C.

B was from liquor not oxidized, but nitre added in the boat pans, and boiled to 138° C.; it was 96° Tw. at 11° C.

The Finishing.

The "finishing-pots" for caustic are made of various shapes, with an upper diameter of 7 feet to 9 feet 6 inches and a depth of 4 feet to 5 feet 6 inches. The usual size is about 9 feet wide and 5 feet 6 inches deep; and they then hold 10 tons of caustic. The thickness of metal in the bottom varies from 2 inches (small pots) to 3 inches (large ones). Much depends upon the proper mixture of cast metal which best resists the chemical action; and in moulding and casting also the utmost care must be employed.

Nearly all the caustic-pots in England are supplied by Messrs. R. Daglish and Co., of St. Helens, and by the Widnes Foundry Company. Figs. 246 to 249 show three of the most usual forms of pots on a scale of 1 : 48 : figs. 246 and 248 are perpendicular sections : figs. 247 and 249, half-plans.

Fig. 246.

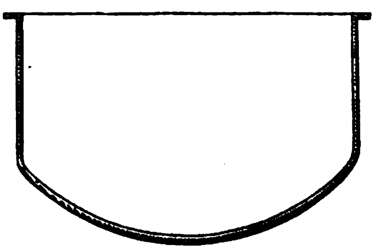


Fig. 247.

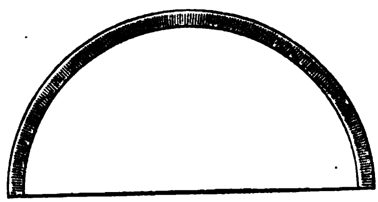


Fig. 248.

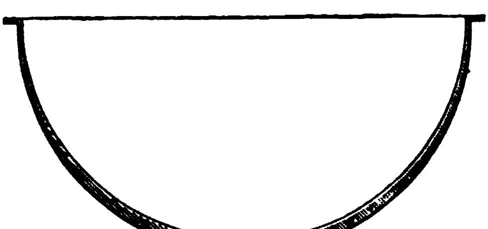
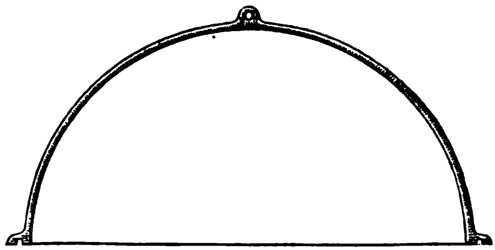


Fig. 249.



A well-made and properly set pot lasts at least ten months, in favourable cases two years, and turns out 600 or 700 tons of caustic, but only if it is turned a little every three months so that fresh places are exposed to the fire. The pots are usually destroyed by a certain place being burnt out too much, where a hole or crack is formed, usually a foot or two above the bottom. The wear and tear is never uniform, but in patches or scars of $\frac{1}{4}$ to $\frac{1}{2}$ inch depth. The pots are nearly always protected from the direct fire by a curtain wall, which divides the flame into two parts; these pass round the pot, and unite again on the opposite side. This setting will be easily understood from figs. 250 and 251.

Fig. 250.

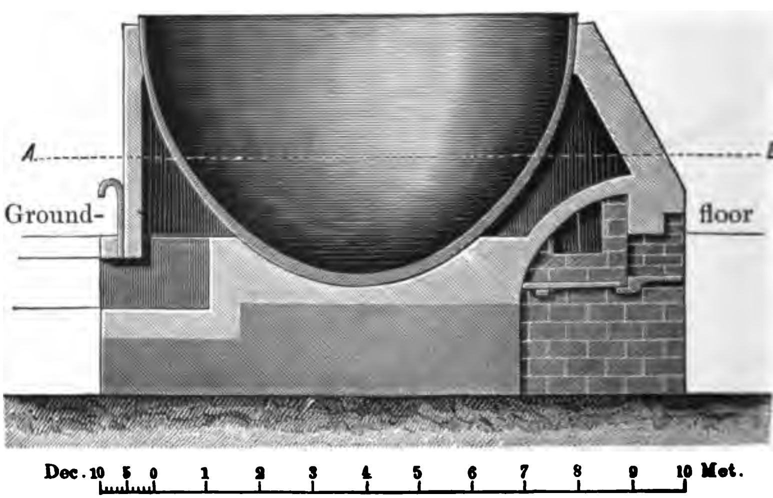
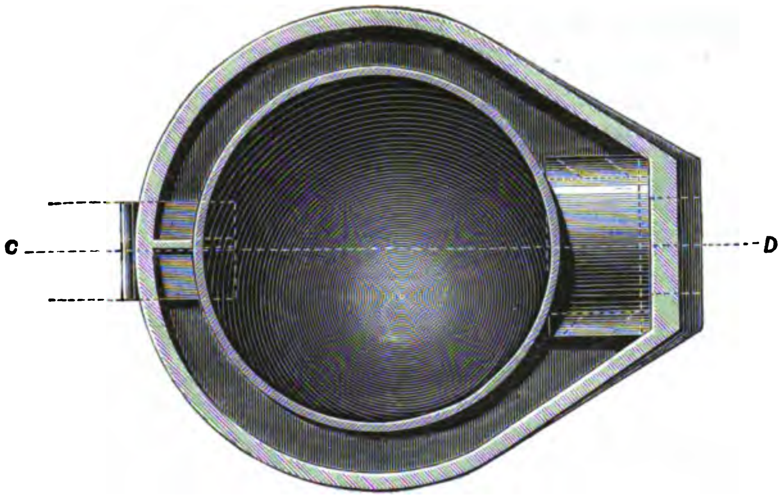


Fig. 251.



The pots are mostly placed on a cast-iron plate, in order to facilitate their turning, for which purpose also three lugs are cast on them at equal distances (fig. 249). Since the weight of a pot itself is about 6½ tons, this turning is always troublesome; in large works it is greatly facilitated by a travelling crane which can be brought over any pot.

Heating the pots by means of gas-producers has been tried, but given up again on account of the great waste of fuel.

Each pot has mostly a sheet-iron cover, frequently balanced by a chain, pulley, and weight; it is only put on during the last stage of the process. The cover has a small opening on one side for introducing the nitre, and sometimes another connected with a tall chimney. Occasionally three pots in succession are employed, one of which is fed with strong liquor from the pans, the second from the first, and the third from the second. But most frequently the liquor coming from the strong- (boat) pans is finished in the same pot.

These pots are now filled with liquor boiling at 138° C., either direct from the boat pans or by baling from another pot; and the liquor is boiled up to 160° C. Between 143° and 160° a scum forms on the surface of the pot, sometimes of a red, sometimes of a black colour: this is removed, by means of perforated scoops, when 70-per-cent. caustic is to be produced, and even for 60-per-

cent. caustic at most works. It has the same composition whether nitre has been added or not:—

	A.	B.
Iron peroxide	traces	traces
„ sulphide	0·139	0·346
Sodium sulphite	51·408	57·120
„ hyposulphite	none	traces
„ sulphate	6·831	5·377
„ chloride	5·265	6·172
„ silicate	0·225	traces
„ aluminate	traces	traces
„ carbonate	15·408	13·013
„ hydrate	20·800	17·672
	100·076	99·700

A was from liquor boiled to 160°: the liquors became oxidized during the causticizing; but no nitre was added in the pans. *B* had had nitre added in the boat pans. Both samples had been dried and pressed before analysis.

These salts are in some works put into the black-salt mixing as they are; in others they are first washed with weak liquors; in others, again, they are put into the strong-pans, where the sulphite, sulphate, and carbonate sink down with the other salts, the chloride and caustic being dissolved.

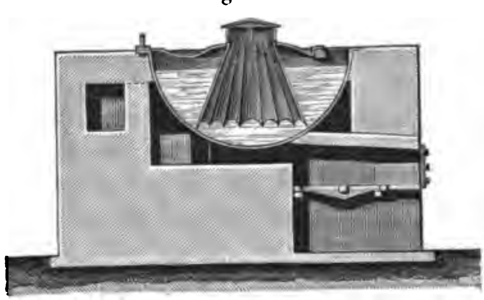
If the production of 70-per-cent caustic is desired, it is best to discontinue firing when the contents of the pot have arrived at 160° C., and to allow them to settle. Chloride, carbonate, and sulphite now settle out, as shown in the following analysis:—

Iron peroxide	1·054
Sodium sulphite	3·603
„ hyposulphite	0·442
„ sulphate	1·146
„ chloride	41·535
„ silicate	0·174
„ aluminate	0·544
„ carbonate	11·488
„ hydrate	19·840
Water (by diff.)	20·174
	100·000

Sometimes 70-per-cent. caustic is made on the plan of separating the salts in one operation. In this case the liquor from the black-ash boat pans is boiled directly to 160° C., and allowed to settle from 12 to 24 hours, after which the supernatant liquor is baled off for finishing.

The boiling of the liquor is then continued; and when the temperature has reached 180° C., it will solidify well on cooling and will contain about 53 per cent. of alkali. It is now darker and more tough and treacle-like; from this point it exhibits a great tendency to boiling over, which is kept down by the attendant by beating in a peculiar manner with his fishing-shovel on the surface of the liquid, thus abating the frothing. It is less troublesome, but decidedly objectionable, to add some oil or grease. Now and then it happens that suddenly the largest portion of the contents of the pot is thrown out of it with the force of an explosion, especially when fresh liquor is added and the salts have not been completely settled out. According to Payen's 'Précis' (1877, i. p. 474), in these pots inverted sheet-iron funnels may be used, 3 feet wide at the bottom, 14 inches at the top, with a nicked-out edge, resting about 2 inches above the pot-bottom, in order to cause the froth, collecting in the lower part of the funnel, to burst in the upper part, and to compel the liquid to run over the upper plate (to which the funnel is attached) into the pot itself. When the mass becomes tougher, this funnel must be taken out. The author has never seen this contrivance applied to caustic-pots, and cannot tell whether it is actually used or not. It is shown in fig. 252.

Fig. 252.



When the temperature has arrived at 205° the boiling ceases almost entirely; and very little steam is given off now, although

there is still nearly 20 per cent. water present. About 238° C. the mass contains almost exactly 60 per cent. alkali, at 243° 61 per cent., at 260° about 64 per cent. alkali.

About this stage the contents of the boiler show next to no motion except a slight boiling round the edge of the pot, and their temperature rises quickly beyond the range of the mercurial thermometer. The steam still given off carries away small particles of caustic, which have an extremely disagreeable irritating effect on the skin; besides, through the action of the caustic soda upon organic matter, a peculiar pungent substance is generated, which forms a kind of smoke; and the surface of the pot becomes covered with a shining scum of graphite, whilst round the edge a separation of reddish salts takes place. The formation of graphite was first noticed by Pauli; it is due to the destruction of the cyanogen compounds occurring at this stage. Now the cover is put on the pot and the heat increased as much as possible, which causes a portion of the graphite to be burnt again. When the heat has got up sufficiently, the complete oxidation of the sodium sulphide and sulphite is effected, either by nitrate of soda or by injection of air. In both cases a trace of unoxidized sulphur is purposely left in, because after its complete oxidation to sulphate green sodium manganate would be formed; or the green colour already formed is destroyed by adding a little sulphur or sodium hyposulphite.

When working with *nitrate of soda*, this is put in gradually, about 2 lb. at a time, through the hole in the corner of the pot. At first its effect is very energetic; and it often deflagrates as soon as it touches the surface of the mass; as soon as the evolution of gas has ceased, more may be added. Afterwards the addition must be made with great caution; and frequent samples must be drawn, solidified by cooling on an iron shovel, and a few drops of a solution of lead acetate poured over them. When the caustic is only just coloured faintly brown by this, the further addition is stopped. The whole operation usually lasts five or six hours. With good liquors (from tank-liquor), on the whole not above 40 to 45 lb. of nitre per ton of caustic are consumed, including that which has been added in the pans.

When working by *a current of air*, a small blowing-engine with short stroke for moderate pressure must be employed; and when water is used in the blowing-cylinder for lubricating the piston, a vessel for catching all water carried away must be attached to the

delivery-pipe; and under no circumstances must water be allowed to get into the pot. The blowing-engines usually employed in Lancashire have a 12-inch cylinder and 12-inch stroke, which is sufficient for supplying three pots with compressed air. The delivery-pipe is 2½ inches wide, and is provided with a cock and a 1½-inch branch for each pot. When a pot is ready for blowing, a 1½-inch iron tube is introduced into it, ending below in a perforated ring or a branch pipe 18 inches long, till it rests on the bottom of the pot; on the top it is connected with the corresponding branch of the air-pipe by means of an india-rubber pipe and a coupling screw. Before the engine is started, the blow-off cock is opened to remove any collected water, and then the communication with the pot is made. The contents of this are put into violent commotion; and after two or three hours their temperature has risen to a red heat. If the liquor was good and some nitre has been put into the boat pans, three or four hours blowing is sufficient; if no nitre has been added, eight hours are required; with bad liquor, resulting from bad black ash or careless lixiviation, much more time may be needed (36 hours even). By too long blowing, as well as by too much nitre, the mass becomes green; and this is likewise remedied by a small piece of sulphur or by careful addition of a little liquor from a neighbouring pot. According to Morrison, for this process 10 per cent. more pot space is needed than for oxidizing by nitre, on account of the violent commotion from the current of air. But this does not seem to be correct: the air rises up in minute bubbles; and boiling-over is even more easily avoided than with nitre. For a ton of caustic, from 24,000 to 30,000 cubic feet of air are required.

Whether in this operation the sulphide passes through the stages of sulphite and hyposulphite can hardly be decided; it is scarcely probable that hyposulphite can exist at so high a temperature. In any case sulphate is the final product. The process may be represented either by Davis's third equation, or by that of Pauli, without the water; Davis's is

$$5Na_2S + 8NaNO_3 = 5Na_2SO_4 + 4Na_2O + 8N\ (?).$$

It is usually assumed that half of the weight of nitre employed is recovered as caustic; and since the value of the latter is nearly always higher than that of the nitrate of soda, it will sometimes pay better to work with the latter, and sometimes to work with the

blowing-engine. The alkalimetrical test, owing to the oxidation of the sodium sulphide, is lowered by 1 or 2 per cent. with nitrate, a little more with blowing. Under exactly equal conditions some works desulphurize the caustic by blowing, others by nitre. In England the former process is much more usual than the latter; on the Continent it is also the more usual of the two. In addition to blowing, some factories use a little nitrate, others none at all. For "cream caustic" from mother liquors (see below) nitrate only must be used.

Shanks (patent Dec. 22nd, 1863) proposed economizing nitre in another way. He runs the liquor, boiled down to 70° Tw. (that is, just on the point of separating salts), upon a sufficient quantity of quicklime to absorb it completely and form a thick paste with it. For each 54 parts alkali, calculated as Na_2CO_3, 42 parts of quicklime are required. A violent reaction ensues. Now the mass is put into a calcining-furnace and treated by heat and air just as if soda ash had to be carbonated; by this the sodium sulphide is oxidized to sulphite. When the mass has become dry, it is withdrawn from the furnace, stirred up to a paste in a vessel provided with an agitator by the assistance of water and steam, and left in till it is completely causticized. Then it is filtered by means of a vacuum and further evaporated as usual. This process was carried out on a large scale at Shanks's works for some time, but abandoned again because there was still ½ to 1 per cent. of nitre required, and the saving of nitre could not make up for the considerable extra expense of the process.

Still less would this be expected from Ordway's process (Wagner's Jahresb. 1859, p. 156). He adds to the liquor a large quantity of finely divided ferric oxide, brings it to dryness, stirs it round for several hours in a dark-red heat, till all is oxidized and the red colour of the ferric oxide prevails; then water is added again, to produce a liquor of spec. gravity 1·273; and this is finished in the ordinary way. Even here 1 per cent. nitre had to be added. The ferric oxide in this case is to act as a porous substance for preventing the fusion of the mass, and accordingly must be employed in large quantity. It is doubtful if this very costly plan has been so much as tried on a large scale.

When the oxidation is finished, a sample is taken, most conveniently in a mould such as is used by pharmacists for sticks of caustic potash, and examined for its amount of total alkali. For

60-per-cent. caustic it ought to test 64 to 70, for 70-per-cent. 70 to 72 degrees of available soda. The colour of the mass varies, according to the mode of working, from a light brown to a deep red. Davis gives the following complete analyses (A from a pot at a works where the solution of the bottoms had been introduced into the operation-pan, B from the same works when the bottoms had been sold separately and thus not re-introduced into the process):—

	A.	B.
Sodium hydrate	82·193	83·566
„ carbonate	2·404	3·174
„ chloride	6·000	8·664
„ sulphate	7·337	3·629
„ silicate	0·284	0·223
„ aluminate	1·216	0·231
„ sulphide	0·018	0·025
Insoluble	0·492	0·386
	99·944	99·898

According to the result of the analysis common salt is added, in order to reduce the strength to the degree intended; the boiler is then brought to its full heat again and allowed to settle. The salt decrepitates violently when coming into contact with the red-hot mass, and makes the caustic spirt about—extremely annoying the workmen and compelling them to wear veils and gloves during this operation. If the cover is taken off now, the graphite can be seen like a brilliant metallic film on the surface; but after the re-heating of the mass, which is necessary for its settling after being cooled by the introduction of the salt, the graphite assumes the shape of coke-like particles floating here and there on the red-hot mass. Ultramarine also appears now, as an amorphous blue deposit, on the edge of the pot and its cover.

Now follows the *settling* in the pot, during which, according to Ralston's patent, the ferric oxide is deposited at the bottom. According to Pauli, caustic liquor, even after dilution, retains ferric oxide in solution to the amount of $\frac{1}{7000}$ of the weight of soda; but fused sodium hydrate cannot do so. The caustic liquor seems not only to act upon the ferric oxide (the rust), but even on the metallic iron itself; the latter is contradicted by most other

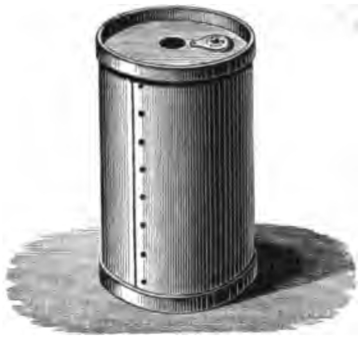
observers, *e.g.* Kolb. At the same time with the iron the alumina is precipitated, either as silicate (Pauli) or as soluble sodium aluminate (Davis), and is deposited along with the ferric oxide. That sodium aluminate is insoluble in strong caustic and is separated along with the bottoms, is confirmed by Morrison.

The time required for settling is from six to eighteen, usually from eight to twelve hours; and during all this time a strong fire is still kept up. The quality of the product entirely depends on the completeness of the settling. In some works it is continued till a thick crust has formed upon the surface of the pots, before packing is commenced; this, however, can only be done when there is pot-room to spare. Some pots absolutely refuse to settle well, generally when there is a minimum amount of iron oxide in suspension along with the tough sodium aluminate. According to Davis this happens most readily with liquors completely oxidized in causticizing, in which the sodium sulphide has been oxidized to hyposulphite and cannot subsequently dissolve the iron of the pans to ferro-sodium sulphide. An excess of ferric oxide causes good settling; hence Davis proposes introducing some iron oxide when the temperature has risen to 205° C.; but his proposal does not seem to have been carried out in practice.

Sometimes it happens that a pot, although clear when well fired, assumes a milky tinge on cooling, and afterwards a portion in the drums will be found slightly discoloured; on solution in water a small quantity of a white precipitate is obtained, sometimes becoming brown by exposure to the air, and consisting chiefly of alumina and lime coloured by minute traces of manganese or iron. This can only happen when, from badly settled liquor or otherwise, lime has been admitted inadvertently.

After sufficient settling in the pot, *packing into the drums* commences. These are sheet-iron casks, of the shape shown in fig. 253, 1 ft. 8 in. wide and 2 ft. 4½ in. high without, or 2 ft. 8 in. with the hoops binding the ends. At the top they have a round hole for filling, afterwards closed by a cast-iron slide, generally marked with the name of the firm. Besides, there is a small hole, through which the air escapes on filling, and which permits the progress made in filling to be observed. The joints are made good with plaster of Paris. Such a drum weighs 21 lb., and holds nearly 6 cwt. of caustic. It is emptied either by knocking off the hoops and rivets, whereupon the whole block falls out in a piece, or by

Fig. 253.



opening the slide and steaming out. In Germany the packing described on p. 593 is usually preferred.

Two or three rows of such drums are placed round the pot, and they are filled one after another by means of a sheet-iron shoot, into the wider end of which the fluid caustic is poured by means of a scoop. If the article does not run entirely transparent and colourless out of the scoop, but shows the least opacity, it is not up to the standard; even if a sample taken from the top be quite good, the centre of the drum will be of a dirty-grey colour. The drums should not be filled up all at once, but in three or four portions; otherwise on cooling a hollow space will be formed in the axis of the drum, taking away about one tenth of the space, and causing an extra cost of 1*s.* 6*d.* to 2*s.* per ton of caustic for packing. Glendinning and Edger (Chem. News, xxvii. p. 199) assert that the composition of caustic is not the same in all parts of the drums; three samples which were taken, *a* 1 inch from the outside, *b* about 5 inches nearer the centre, and *c* from the centre itself, showed on analysis—

a.	*b.*	*c.*	
66·9	69·7	61·6	per cent. available alkali,

while the sample taken during the packing, and consequently reliable, showed 66·8 per cent., thus being identical with the outer crust of the block. They ascribe this difference to the circumstance that, on solidifying, the water has a greater affinity for the liquid

than for the solidified portion [this is very questionable !], and consequently accumulates in the centre, which solidifies last. Morrison entirely denies the difference of quality within the same drum; he never found more than 0·2 per cent. difference in testing any portion of a block.

When, in packing, the lower portion of the pot is reached, great care must be taken. As soon as the mass becomes in any way of doubtful quality, the packing is discontinued, and the doubtful portion baled over into a neighbouring pot till the proper *bottoms* are reached. These are but rarely of a sufficiently light colour to be also baled over into another pot. Moreover the iron and alumina must be removed at some stage of the manufacture; it is therefore much more usual to pack the bottoms (which amount to 9 or 11 per cent. of the caustic produced) into separate drums and sell them as such, or, if they do not fetch a reasonable price, to pour them into iron boxes, break them up after cooling, and redissolve them. This is done in a special small tank by the help of steam; and all the strongly alkaline fished salts and other by-products are added; the solution is brought to 48° Tw., completely settled, and the clear liquor either added to the liquor in the operation-pan or treated as indicated lower down. The residue, chiefly consisting of ferric oxide, is thrown away.

The following is the composition of the bottoms of 60-per-cent. caustic, according to Davis :—A, from a pot very red before salting; B, from a pot the liquor of which had been thoroughly oxidized during causticizing; C, from liquors only partially oxidized during causticizing. The analyses show what becomes of the alumina and iron :—

	A.	B.	C.
Insoluble matter...	23·000	1·948	4·664
Sodium hydrate ...	58·888	70·896	71·886
„ carbonate .	trace	none	0·722
„ chloride ...	6·135	14·040	10·729
„ sulphide...	0·132	0·054	0·116
„ sulphite ...	0·151	0·063	0·074
„ sulphate...	5·534	8·526	4·624
„ silicate ...	0·683	trace	trace
„ aluminate .	5·661	9·556	7·133
	100·184	100·083	99·928

Composition of the insoluble matter of A and C:—

	A.	C.
Graphite	2·146	1·179
Iron peroxide	93·000	94·006
Calcium oxide	4·332	4·289
Manganese oxide, magnesia, &c.	0·522	0·526
	100·000	100·000

The bottoms are usually sold on the basis of 54 per cent. alkali; and if they test more they are reduced to 54° by fished salts.

A peculiar way of packing caustic very much in favour in America, especially for making soap in households, is in tin canisters of 1 lb. each, or in balls with a covering of rosin. The Philadelphia Salt-Manufacturing Company at Natrona, near Pittsburg, who introduced the caustic thus packed as the "Patent Saponifier," in 1875 sold 10,400,000 pieces. The canisters are made by special machinery, and, after filling and soldering up, are protected against rusting by a film of carbon, produced by dipping a number of the canisters at a time by means of a wire netting, into petroleum, which is then burnt off, leaving a closely adhering thin film of soot on the metallie surface (Goldschmiedt, Austrian Reports on the Philadelphia Exhibition, vol. vii. p. 16).

The analyses by Renner and Reichardt (from Knapp's 'Chem. Technologie,' i. 2, p. 458) refer to products quite unsaleable in England, and now-a-days also in Germany. Those of Renner are very suspicious, from the total absence of sodium chloride.

In England every thing is calculated as "alkali" which neutralizes the test-acid—that is, especially also the carbonate, of which, however, usually a maximum of 2 or 3 per cent. is stipulated. In Germany the carbonate is not paid for at all, and only the real caustic is reckoned, but (very strangely) expressed in parts per cent. of carbonate, as mentioned on p. 546.

Commercial white caustic is composed as follows :—

	60-per-cent. caustic (Davis).		70-per-cent. caustic (Davis).		60-per-cent. caustic (Morrison).	70-per-cent. caustic (Morrison).	Renner.	Renner.	Reich-ardt.	60-per-cent. caustic (Tyneside).
Sodium hydrate	72·774	75·246	83·840	89·600	70·0	82·0	72·89	64·14	53·33	75·00
„ carbonate ...	1·419	2·536	4·686	2·481	6·0	5·0	9·20	4·11	......	1·50
„ chloride	18·800	17·400	6·522	3·919	18·5	7·0	......	......	......	9·80
„ sulphate	6·462	4·398	4·526	3·419	5·5	6·0	14·90	27·53	33·28	10·38
„ sulphite	......	......	......	......	......	......	......	......	......	0·80
„ sulphide	0·063	0·027	0·025	0·025	......	......	......	......	......	0·30
„ silicate.........	0·304	0·297	0·463	0·304	......	......	......	......	......	0·44
„ aluminate ...	trace	trace	trace	trace	......	......	......	......	......	0·31
Water in excess	......	......	......	......	......	......	1·53	3·12	10·50	} 1·47
Insoluble	......	......	......	......	......	......	1·48	1·03	1·23	
	99·822	99·904	100·062	99·748	100·0	100·0	100·00	99·93	98·34	100·00

Whether the following analyses, by Tissandier (Monit. Scientif. 1868, p. 909), refer to white or cream caustic, is not stated; the "English" caustic, to judge from its strength, seems to have been white.

	French Caustic.			English Caustic.			Inferior Caustic.		
Water	4·38	3·31	3·71	0·59	0·68	1·11	1·01	0·92	0·99
Sodium chloride	11·32	12·22	3·90	7·23	6·89	5·60	18·86	19·76	17·47
„ sulphate	3·41	2·00	2·60	1·00	1·32	2·10	7·42	3·09	2·36
„ carbonate ...	5·58	9·82	3·69	3·45	3·68	5·48	6·48	34·63	38·37
„ hydrate	75·21	72·65	86·10	87·73	87·50	85·71	66·12	41·60	40·81
Total	99·90	100·00	100·00	100·00	100·07	100·00	99·89	100·00	100·00
Percentage of Na_2O...	58·10	56·30	66·67	68·00	67·80	66·40	51·24	32·24	31·60

The last two analyses of inferior caustic refer to an article which ought not to occur in commerce at all. The percentage of available alkali is not calculated in the English way (from caustic and carbonate together), but in the German way (from caustic only). Tissandier's analyses are rendered suspicious by the fact that they do not mention any oxidizable sulphur compounds, nor silica aud alumina, and yet all sum up to 100·00, the water having been estimated directly: the exceptions to the above are not shown in Tissandier's Table (where they are all summed up to 100·00), but come out as such on adding up the items. For ordinary commercial analyses an estimation of the total alkali and that of the real caustic are sufficient, according to p. 545. As a check, in the washed precipitate, containing carbonate and sulphate, the carbonate can be estimated by dissolving in standard hydrochloric acid and titrating back with standard soda.

Messrs. Gaskell, Deacon, and Co., at Widnes, for some time manufactured *crystallized caustic* according to a patent of Deacon's (April 10th, 1862), by drawing off the liquor before it reached the stage at which it would solidify on cooling, at a boiling-point of about 177° C., cooling down to 70°, and allowing it to crystallize for a long time at 48° in thin cast-iron boilers provided with a

plug-hole in the bottom. The crystals were separated from the mother liquors, melted up again, and packed as usual in iron drums. Their quality was very fine; the composition of this caustic was—

Na_2O	50·5
$Na_2S_2O_3$	0·5
NaCl	1·8
H_2O	47·2
	100·0

In spite of the purity of the product, this manufacture has had to be given up again, because it did not pay.

Hermes (Deutsche chem. Ges. Ber. iii. p. 122) during a hard winter obtained from a strong caustic liquor (spec. grav. 1·365) fine, glass-like, transparent colourless prisms, melting at 6° C., showing the specifie gravity 1·405 and containing 30·09 per cent. Na_2O, corresponding to the formula $2NaOH + 7H_2O$.

Cream Caustic.

This is sometimes made direct from tank-liquor, but mostly from *red liquors*. From these also by special care *white* caustic can be made by fishing for a longer time, keeping the temperature before the last settling as high as possible, and waiting long enough (till the pot is covered with a thick crust) before packing. Thus at Aussig all the red liquors are worked up into white caustic of 73 per cent. available soda as caustic only (without the carbonate), without any previous oxidation by a current of air, and without any nitre whatever; all the oxidizing is done by blowing during igneous fusion. Often red liquor and tank-liquor are mixed together, causticized by lime, and worked in the usual way for 70-per-cent. white caustic. But mostly from red liquors only cream caustic is made, along with the solution of the bottoms previously mentioned, and sometimes also with a little tank-liquor. Causticizing with lime is not necessary, as the red liquors are caustic enough without that. We have previously given analyses of such liquors; but we subjoin another analysis (by Davis) of a red liquor directly before working up for caustic of 62° Tw.

Iron sulphide	0·313
Sodium bisulphide	0·195
„ sulphide	6·256
„ sulphite	16·022
„ hyposulphite	7·858
„ sulphate	14·848
„ chloride	65·526
„ silicate	9·677
„ aluminate	1·031
„ carbonate	79·966
„ hydrate	194·400
„ sulphocyanide	0·261
„ ferrocyanide	0·423
Grams per litre	396·776

The completely settled red (or other) liquors are boiled down in a long wrought-iron pan, separately fired, and the salts fished out from time to time. When the contents have reached 70° Tw. or the temperature 121° C., the pan is allowed to cool and the salts are well fished out. The fire is applied again; about 2½ to 3 cwt. of nitrate of soda per ton of caustic are added; the boiling is continued till 94° Tw. or a temperature of 132° C. has been reached; a little more nitrate is added, in case the first quantity was not sufficient; the liquor is allowed to cool for one or two hours, and run into a settler. The remaining salts are washed with a little water (which may be added to the next portion), in order to remove the nitrate; they are now taken out, drained, and worked up for "caustic ash." When the liquor has been causticized by lime, nothing like so many salts are separated, and cast-iron boat pans may be employed. The completely cleared liquor is run into a caustic-pot. It has a dark straw-colour, and on boiling gives out ammonia in large quantity. All the nitrate is added from the first, in order that no more of it may be required in finishing. Blowing by air is not applicable for cream caustic, because the temperature does not rise sufficiently for that. The contents of the pot are carefully concentrated till they have attained the usual strength of cream caustic (60 per cent.). As igneous fusion is never reached, this article contains much water.

Now and then (but only with careless firing) a batch becomes red; and as it is not possible to remedy this in the same way as with white caustic, the temperature not being high enough, the whole must be packed as it is, and sold for what it fetches; or the heating must be continued up to igneous fusion, and white caustic made of it. For the same reason, no "bottoms" are separated, but the whole contents of the pot are packed right away, beginning directly after the boiling has ceased.

Morrison states that the usual composition of cream caustic is

$NaOH$	70·0
Na_2CO_3	5·0
$NaCl$	7·0
Na_2SO_4	2·0
H_2O	15·8
Insoluble	0·2
	100·00

Factitious Potash.

Under this extremely inappropriate name is (or was) sold a product which was to imitate American stone ash. It varies in colour from red or pink to yellow, and is obtained by carrying on the concentration of the caustic-soda liquor only so far that it just solidifies on cooling. It readily attracts water, of course, and melts very easily. Often it is mixed with two thirds of its weight of common salt; and the red colour is, if necessary, artificially given by adding during the concentration 1 per cent. of sulphate of copper and stirring round with a wooden pole, so that red cuprous oxide is formed. Of course this article is only sold by unscrupulous dealers, and bought by very ignorant consumers. It is said to have been first made by a French manufacturer of the name of Ador.

Costs.

In the direct manufacture of caustic from tank-liquor, with rationally conducted work a yield of 54 to 57 parts of 60-per-cent. caustic on the sulphate is reckoned, including the bottoms, which amount to 9 or 11 per cent. of the caustic; with red liquors they amount to 12 or 14 per cent. Of common salt for reducing to 60

per cent. 15 or 16 parts to 1000 of finished caustic are required; of nitrate of soda 1½ to 2 parts, half of which is recovered as caustic.

The total consumption of coals, according to Morrison, in some works exceeds 7 tons for each ton of caustic, but in well-managed works need not exceed 6 or 6½ tons; it is distributed as follows:—

Black-ash furnaces, mixing-coals	1 ton.
„ „ firing-coals	2 tons.
Boat pans	2 „
Caustic-pots	1 ton.
Steam-boilers	½ „
	6½ tons.

For cream caustic from red liquors a good deal of the cost of concentration is saved, since liquor of 60° Tw. is commenced with; but, on the other hand, at least 5 per cent. of nitrate of soda on the caustic are consumed.

The wages are stated by Morrison as follows for a ton of 60-per-cent. caustic (in 1874):—

	£	s.	d.
Black-ash men (at 5¼*d.* per ball)	0	5	3
Mixing and laying down at furnaces	0	2	6
Wheeling coals and ashes	0	2	0
Attending the tanks and the tank-waste	0	2	8
Spare black-ash men (wheeling fishings &c.)	0	1	3
Steam-boilers	0	1	8
Foreman	0	3	0
Operation-pans	0	2	4
Boat pans	0	2	6
Finishing-pots	0	4	0
Filtering	0	1	4
Weighing	0	1	6
Unloading and loading (2¼*d.* per ton)	0	2	8
Yard labourers	0	2	0
Carry forward	1	14	8

	£	s.	d.
Brought forward	1	14	8

Besides, for Repairs:—

	£	s.	d.	£	s.	d.
Blacksmiths	0	1	6			
Carpenters	0	0	10			
Bricklayers	0	1	6			
Fitters	0	1	6			
				0	5	4
				2	0	0

The total costs in 1874 (when every thing was very dear) are stated by Morrison as, per ton of 60-per-cent. caustic:—

		£	s.	d.	£	s.	d.
Coals, 6¼ tons	at	0	7	0	2	5	6
Sulphate of soda, 1 ton 17 cwt.	„	3	5	0	6	0	3
Limestone, 1 ton 2 cwt.	„	0	6	8	0	7	4
Lime, 11 cwt.	„	1	0	0	0	11	0
Salt, 3 cwt.	„	0	13	4	0	2	0
Nitrate of soda, 40 lb.	„	0	0	1½	0	5	0
Wages					2	0	0
Water					0	1	6
Packages					0	16	0
Loading and shipping					0	15	0
Office expenses and management					0	5	0
Interest on capital, writing off, small stores, &c.					0	16	0
Total cost (free on board) at Liverpool					14	4	7

More favourable in the more important points are the following figures, obtained from a trustworthy source, upon the materials and wages required for 1000 tons of 60-per-cent. caustic:—

	Ordinary work.	Excellent, but actual, work.
	tons.	tons.
Coals	5750	5271
Sulphate of soda	1825	1760
Limestone	625	520
Lime	875	891
Nitrate of soda	21¼	21¼
Salt	75	64
Wages	£2000	£1500

The greatest *consumption* of caustic is in soap- and papermaking, especially for straw-, Esparto-, and wood-pulp, less so in bleaching fabrics. It is used in manufacturing oxalic acid, and recently in the manufacture of alizarine, resorcine, and other hydroxylated compounds obtained by alkaline fusion, for purifying mineral oils, &c.

The manufacture of caustic soda has very much increased of late. In 1867, on the Tyne, 3720 tons were made, in Lancashire 11,213 tons; since then the production has at least doubled. In Germany in 1872 in nine works 1165 tons, but in 1875 already 6165 tons were made.

CHAPTER XIV.

TANK-WASTE.

When describing the lixiviation of black-ash, we mentioned the residue insoluble in water which has at last to be removed from the tanks to make room for more black ash. This residue (tank-waste or vat-waste) is a source of great inconvenience to alkali-makers, so much so that perhaps most of the proposals for other processes than Leblanc's have been occasioned by it: What appearance fresh tank-waste ought to have, we have already seen (p. 479). In this damp state it is a dark grey or black mass, chiefly consisting of calcium monosulphide, with an excess of calcium carbonate and hydrate and a series of other matters, as the subjoined analyses (Table, pp. 634, 635) show. Its dark appearance is partly caused by unburnt carbon, partly by iron sulphide.

It is hardly necessary to mention that the grouping of the constituents on the part of the different analysts is quite arbitrary. The sodium, for instance, is once quoted as sulphide, once as carbonate, and once as aluminium sodium silicate; no one quotes it as calcium sodium carbonate, the existence of which Scheurer-Kestner has rendered very probable. The analyses also ought to distinguish between the portion soluble and that insoluble in water. The hypothetical calcium oxysulphide in all these analyses has been calculated into CaS and $Ca(OH)_2$.

The damp waste soon *changes in the air*, under the influence of oxygen and carbonic acid, more or less quickly according to circumstances, but always with evolution of heat in consequence of

its oxidation. With large quantities the heat of tank-heaps increases in a few days so much that the heap becomes red-hot. As in the meantime sulphur has been separated, this burns, and the smell of SO_2 is very perceptible. Along with this, owing to the action of atmospheric CO_2 on the soluble calcium sulphides, and more so of the SO_2 and SO_4H_2, evolution of H_2S sets in. We have already (p. 454) seen how the oxidizing process must be understood, and what part ferric oxide plays in it From the insoluble CaS are formed soluble calcium sulphhydrate, polysulphides, hyposulphite, and the corresponding sodium compounds, besides insoluble calcium sulphite and sulphate. The latter decomposes any sodium carbonate into sodium sulphate (which is sometimes found as an efflorescence) and calcium carbonate. The oxidizable sulphur compounds of calcium and sodium are then further oxidized, the hyposulphite with separation of sulphur, which partly crystallizes out as such, similarly as in solfataras, partly makes more CaS soluble by the formation of polysulphides. Kuhlmann found in tank-heaps beautiful gold-coloured crystals of $CaSO_3 + 2\,CaS + 6\,H_2O$.

Finally there ought to be nothing present but calcium carbonate and sulphate, sodium sulphate, calcium and aluminium silicate, ferric oxide, coal, and other indifferent and entirely harmless matters. But it takes many years before the oxidation of large heaps is finished. Even after 30 or 40 years unoxidized sulphur is found in the interior of such heaps, which thus may yield yellow liquors (see below).

Dr. Smith (Inspector's Report, 1877–78, p. 42 *seq.*) found that, on passing air through a magma of gypsum and calcium sulphide with very little manganese peroxide, all the sulphate was destroyed, hyposulphite being formed. According to him, even sulphites cannot be formed as long as calcium sulphide remains to prevent an excess of oxygen. If the latter be in excess, sulphite and sulphate are formed, but are reduced to hyposulphite in passing through the heaps of tank-waste, where they meet CaS. Dr. Smith thinks it possible thus not only to obtain the sulphur from fresh tank-waste, but also from the fully oxidized heaps—nay, even from natural selenite. But the details of the process are not clear to himself yet, and he leaves the working-out of this idea to the future.

Owing to the oxidizing processes described, it is out of the question to simply throw the tank-waste onto waste ground,

Composition of

	1. From Ringkuhl. Unger.	2. Brown.	3. Dieuze. Works. Hofmann.	4. Dieuze. Laboratory. Hofmann.
Sodium sulphide	1·78	......	9·94	4·55
„ carbonate	......	1·309	......	......
„ chloride	......	......	0·15	......
„ oxide (Na_2O)	......	......	......	......
Calcium sulphide (CaS)	29·30	24·700	38·00	35·00
„ bisulphide (CaS_2)	4·67	3·583	......	......
„ hydrate	14·85	9·780	14·77	13·75
„ carbonate	19·56	24·220	26·62	21·54
„ silicate	......	......	......	8·97
„ sulphate	3·69	4·281	2·60	......
„ sulphite	......	......	......	......
„ hyposulphite	4·12	trace	......	......
Magnesium silicate	6·91	5·987	......	......
„ oxide or carbonate	......	......	......	......
„ aluminate	......	......	......	2·31
Silica (combined)	......	......	......	......
Iron sulphide	......	......	......	4·22
„ peroxide	3·70	5·716	2·60	......
Alumina	......	......	2·91	......
Aluminio-sodium silicate	......	......	......	......
Carbonate or Coke	2·60	12·709	5·35	2·84
Sand	3·09	5·746	......	3·15
Water	6·05	2·100	......	3·82
Total	100·32	100·131	102·94	100·15

Remarks.—(1) From Liebig's Jahresb. 1847–48, p. 1047. It was evidently partly oxidized. Combined water 2·56, hygroscopical 3·45 per cent. (2) This waste also (from a factory) was partly oxidized. It contains an abnormally high quantity of coal and magnesium compounds. (5 and 6) No coal or sand are mentioned here? (7) From Wagner's Jahresb. 1866, p. 164. This was thoroughly weathered residue. Calcium sulphate, sulphite, and hyposulphite are put in with their water of crystallization. Total water escaping on calcining 10·780 per cent. (7, 8, 9) From Dingler's Journal, cxcii. p. 61. The waste was fresh, but had been completely washed with cold water and dried on a fire-brick slab, by which treatment it had evidently been partly oxidized.

Tank-waste.

5.	6.	7.	8.	9.	10.	11.
Liverpool.		German works.	Saarau works.			South Shields.
Fresh.	6 weeks old.					
Muspratt and Danson.		Petersen.	Richters.			Lunge.
2·87	1·44	......	......	......	......	......
......	......	0·568	......	......	......	3·95
......	......	0·035	......	......	......	......
......	......	......	2·52	2·10	1·89	......
36·70	25·79	8·441	37·62	38·04	39·10	39·42
0·62	5·97	......	......	......	......	......
9·11	6·59	......	6·49	7·00	7·25	9·95
23·42	41·20	36·884	23·18	22·24	24·02	22·64
......	......	......	......	......	......	3·19
4·59	2·53	4·721	1·68	1·01	1·38	trace
......	......	24·180	0·74	0·31	0·63	......
......	......	2·607	2·69	3·02	2·35	......
1·78	3·63	......	......	......	......	trace
......	......	1·742	0·64	0·54	0·70	......
......	......	......	......	......	......	......
......	......	......	4·24	4·03	4·62	......
......	......	......	1·88	1·75	2·01	3·07
7·40	8·91	1·337	......	......	......	......
		......	2·11	2·02	2·00	0·76
......	......	3·676	......	......	......	......
......	......	5·873	5·41	6·00	6·39	2·36
......	......	6·294	7·74	6·82	7·21	13·72
13·51	3·86	3·642	2·32	3·29	1·51	......
100·00	99·92	100·000	99·26	98·17	101·06	99·06

(11) Own analysis of a sample, taken by the author from a freshly washed tank, at once tightly closed up in a bottle and weighed in the damp state with all expedition. The water was estimated separately, and the results calculated upon dry substance, but without any "correction;" in the fresh state the moisture amounted to 31·50 per cent. Thus the real composition of tank-waste as it comes direct from lixiviation was found; hence probably no calcium polysulphides, nor sulphite or sulphate was found. The soda was present partly in the soluble, partly in the insoluble state; it is all calculated as Na_2CO_3. The quantity of sand was abnormally large; but otherwise the waste was completely normal.

perhaps even mixed with burnt pyrites, ashes, rubbish, &c. The smell would soon become a nuisance to the neighbourhood; and especially the drainage of the yellow liquors, through the soluble sulphides being washed out by rain water, would be quite unbearable. This can be remedied to a certain extent, but only very partially, by spreading the waste in thin layers by itself, not mixed with any other rubbish, and beating it to as hard a consistence as possible, covering this layer with another, and so forth. As soon as any cracks appear, they must at once be beaten up with a shovel. In this way, by the hardening of the surface, the decomposition is made very slow and, accordingly, less intense. Thus whole hills have been raised near many large alkali-works; railway embankments, party-walls, &c. have been made from it. But such tank-heaps sometimes take fire, if the oxidation in their interior becomes so violent that large rents are formed through which the red-hot interior can be seen; in this case much SO_2 and H_2S is given off. Such fires are often not easily put out.

These tank-heaps already amount to a great nuisance. They take up very much space, since for each ton of soda ash 2 tons of damp or 1½ ton of dry waste are got—a little less with Mactear's process. But this is nothing when compared with the annoyance caused to the neighbourhood. In dry weather the tank-heaps, unless they are on fire, do not usually smell at all, or very little; but even then sometimes the smell cannot be kept down, and in damp weather the sulphuretted hydrogen infects the air for a great distance. This nuisance in the case of old heaps can be greatly abated by covering them with a layer of fresh soil, or, still better, of burnt pyrites; for new heaps this would require an enormous area. But much worse than the smell of the heaps themselves is the liquid formed by the action of the rain water on the soluble sulphides of the heap, and oozing out at its foot. It is a yellow stinking liquor, which gives off H_2S even by the action of the CO_2 in the air, but much more by that of the air of the drains, which contains much more CO_2, or the acid liquids run to waste from the works. These *yellow liquors* can only be kept under in specially favourable circumstances; wherever they come they cause mischief. If run into a watercourse, they make it entirely unfit for drinking. Even where this does not matter, they still kill all the fish, and and may damage the foundations of houses. When they get into drains which are in communication with occupied dwellings, the

quantity of gas escaping from them sometimes overcomes the slight resistance offered by the water-lutes, and penetrates into the houses, which it renders all but uninhabitable; and in the most favourable case, when the liquor has been completely oxidized, its calcium salts make the well-water excessively hard.

The drawbacks connected with the accumulation of tank-waste were comparatively unnoticed until within the last few years, on the one hand the number and size of the alkali-works having enormously increased, and, on the other hand, the attention of the public and the authorities having been awakened to the importance of the purity of soil, water, and air.

Two questions may here arise:—What can be done with existing old heaps? and what is to be done with the waste arriving from day to day? Even if the latter were got of in some way, the old heaps, especially the drainage from them, call for attention. The question of working up this drainage in a profitable way will be discussed after treating of fresh waste; but sometimes the question is only how to get rid of it somehow without special apparatus. In such a case the author abated the nuisance caused by the yellow liquor getting into the town drains by first purifying the liquor. This was done in three pits, through which the liquor had successively to pass before running away. In these it was mixed with the mud from the manganese-liquor-settlers belonging to Weldon's manganese-recovery process, consisting chiefly of iron hydroxide, a little manganese peroxide, and calcium carbonate. By this it was entirely decolorized and desulphurized; the clear liquor could be run off; and the residue, shovelled up, became available again after some exposure to the air, the atmospheric oxygen, as in the case of the gas-purifying mass, regenerating the metallic oxides with separation of sulphur. We shall see how this can be made a continuous process by mixing the liquor with ferric or manganic hydroxide and blowing air through the mixture; the metallic sulphides formed would thus be constantly oxidized at once to hydroxides and sulphur.

Wherever the question is how to dispose of the *tank-waste obtained from day to day*, one out of many different methods is employed. The most radical is that followed by nearly all the Tyneside works, but only possible in those few localities which are in immediate and near communication with the sea. The tank-waste is carried in waggons to the quay, and tipped by movable shoots

into peculiarly constructed vessels, which take it three miles out to sea and drop it there. The whole central part of the vessel consists of a square space, tapering below, from which the whole vessel has received the name of *hopper*. The sides of this space are lined with sheet-iron; a number of trap-doors, turning on hinges, are drawn up by chains and a winch, and form a bottom for the hopper, but not water-tight. The sides of the hopper are quite tightly joined to the vessel; so that the stem and stern and the passages at each side provide the necessary buoyancy. The tank-waste, when tipped into the central part, displaces the water through the joints of the bottom-doors, of course not completely. Arrived on the high sea, the doors are let down and the waste falls out into the sea, the crew assisting by means of poles. The conical form and the sheet-iron lining of the hopper assist in its emptying. The doors are now drawn up again, and the vessel returns into the river. Such a hopper holds from 140 to 300 tons of waste. Many factories have their own hoppers; others are served by a Company.

Taking the waste to sea is somewhat costly (about 1*s*. per ton), even apart from the expense of conveyance to the wharf. In stormy weather the hoppers cannot go to sea; and great inconvenience arises from this. But most works cannot possibly avail themselves of this plan of getting rid of their waste, and must look out for others. The author knows of a case where the owner of a moderate-sized works, who possessed a good deal of land close to it, had a piece of it dug out to a considerable depth, laid the soil on one side, filled the hole within a yard of the surface with tank-waste, put the soil on the top of it and tilled it again; then a new part of the field was treated similarly. Very good crops were obtained from the newly made soil, nor was the surface drainage troublesome, because the level of the waste was below it; but of course such a thing can only be done exceptionally.

Other applications of tank-waste proposed are equally insufficient for disposing of large quantities. Juncker proposed it as an excellent remedy against dry rot (Dingl. Journ. clxxxiv. p. 543); Lieschning, against the potato- and grape-disease (Polyt. Centralbl. 1863, p. 1242); Deacon, for building, mixed with sand (Dingl. Journ. clxii. p. 279); Kuhlmann, for the same, ground up with burnt pyrites (ib. clxii. p. 46); Varrentrapp, for making footpaths, as a bottom for road-metal, and in the place of ballast between railway-rails (ib. clviii. p. 420); the author, for bottle-glass (ib. ccxvi.

p. 375). Long before all these proposals the waste was used in the factories themselves for making floors. It is spread in thin layers, made into a puddle with a good deal of water, sometimes adding a little salt, and beaten up tight with shovels; it must not be walked on for a few days till it has hardened by oxidation. Such floors become hard enough for ordinary traffic, but cannot even stand wheel-barrows, and are quite inapplicable out of doors; in the open air they are soon converted by the rain into a muddy mass, in which stand yellow and brown pools of sulphur-liquors. Walls made of tank-waste between loose boards (like concrete), are hard at first, but soon become weathered and break up. For this resson they cannot be used for many purposes, least of all for building proper. Even for filling up, tank-waste should only be used where no drainage of liquors can ensue; if this is excluded, even dwelling-houses may be built upon it, as the once hardened waste, if protected from the weather, is entirely harmless. If, however, a building is erected upon it before the oxidation is quite complete, its expansion, consequent upon the formation of gypsum, may cause unpleasant risings of the soil and endanger the stability of the building.

Fresh tank-waste cannot be employed as manure; on the contrary it kills the plants. After complete oxidation, when it has become light yellow or white, it may be taken upon the fields, but is of little value there.

Its employment for *mortar*, mentioned in a former place (Vol. I. p. 264) would possibly afford a pretty good outlet for soda-waste in the neighbourhood of the works. It furnishes an excellent, hard, cement-like, and cheap mortar. Quite different from this is the proposal of Aspden, to employ the tank-waste for Portland cement by calcining, washing, and igniting it with finely ground clay to commencing fusion; here the waste acts chiefly like chalk, but not so well, owing to its impurities. Again another case is the simple employment of desulphurized waste, analogous to Scott's selenitic mortar; we shall see this later on.

A. Smith patented (Oct. 23rd, 1845) the employment of oxidized tank-waste in the place of chalk for black-ash mixing. This has not been done successfully except with desulphurized waste, and even then on only a limited scale (see below).

Undeniably the most rational employments of soda-waste are those founded upon the *sulphur* contained in it. All the sulphur

introduced into the alkali-works as brimstone or pyrites is lost in the course of manufacture; apart from the slight quantity lost in making sulphuric acid, the smaller portion reappears in soda-ash &c. as sulphate, *i. e.* as impurity; the larger portion, viz. 80 per cent. (with revolving furnaces 90 per cent.) of the sulphur is found in the tank-waste, where it is the cause of all the troubles described. Hence nothing is more natural than trying to utilize this sulphur, which cán be done by either obtaining sulphur compounds or brimstone from it.

Interesting, but not practically successful, was J. L. Bell's experiment of making *factitious pyrites* from tank-waste and burnt pyrites (patented Nov. 17th, 1852; Transactions Newc. Chem. Soc. 1869, p. 117). These two materials were smelted in a specially constructed blast-furnace with coke and with addition of common clay (to form an easily fusible slag with the lime of the tank-waste), the blast being heated to 350° C.; a portion of the clay and the coke could be replaced by black-ash-furnace cinders, which contain both. Iron sulphide was obtained, which was tapped from time to time; but difficulties in employing the damp pulverulent soda-waste, which it did not pay to dry, and above all the rapid destruction of the lower part of the blast-furnace compelled a stoppage of the process. For some time 70 tons of factitious pyrites per week were made, with a consumption of 75 per cent. of its weight of coke, and at a total cost (when every thing went well) of 12*s*. 6*d*. to 15*s*. per ton. During the operation H_2S frequently escaped at the top of the furnace, SO_2 rarely. The slag contained much iron, since the furnace had to be worked with strong charges, and consequently not very hot; otherwise along with the pyrites much white pig-iron containing 2 to 2·9 per cent. sulphur, and consequently useless, was obtained. The "factitious pyrites" itself was black on the outside, but inside often of a dark bronze colour with metallic lustre and somewhat crystalline structure. Its percentage of sulphur varied from 25·5 to 33·2 per cent.; on the average it was 30·63 per cent. Besides, oxygen (about 4 per cent.) was always present, because the furnace could not be worked up to complete reduction. About 62 per cent. of the sulphur contained in the tank-waste and the burnt pyrites was recovered as factitious pyrites. It was not easily worked in the burners, owing to its dense texture; and nowadays such a product would hardly be burnt, even if it could be had for nothing: scarcely half of its sulphur

would be burnt off; and coal-brasses had to be burnt along with it. Exposed to the air it fell to powder, and had to be treated in a peculiar way. After 4000 or 5000 tons of this factitious pyrites had been made, the matter was given up again, because the price of natural pyrites had come down again, and it could no longer compete with the latter.

Utilization of Sulphuretted Hydrogen.

Furthest of all from realization has been (until very recently) the idea of utilizing the sulphur of tank-waste in the form of sulphuretted hydrogen. Apart from all proposals for evolving H_2S from the sodium sulphide itself, so as to avoid altogether the formation of tank-waste (Beringer, Hunt, &c.), which belong to another chapter and have been treated of at p. 345, Gossage in 1837 had already taken out a patent for decomposing tank-waste by hydrochloric or carbonic acid and employing the H_2S for making sulphuric acid. The calcium carbonate formed when CO_2 was employed was to go back into the process. Hydrochloric acid could never be seriously thought of for this process, even if it cost nothing, since the decomposition of the calcium sulphide, carbonate, and hydrate in the tank-waste would require much more of it than had been obtained previously in decomposing the common salt. Gossage in reality only intended employing carbonic acid after he had proved that it decomposes calcium sulphide equivalent for equivalent, forming $CaCO_3$ and H_2S. An excess of carbonic acid was to be avoided by passing the gas systematically over fresh waste, for which purpose two towers with several grates were erected. Even in 1854 Gossage was so firmly convinced of the practicability of this idea that he made a contract for a term of years with several Widnes alkali-manufacturers, to treat their waste by this process. But, as we can *now* see plainly (since we have before us the experience of our predecessors), the sulphuric acid produced fell far short of covering the expense; and although, with one exception, all the manufacturers released Gossage from his contract, he had to sacrifice nearly all his fortune to indemnify the one firm that held him to it. The attempt to burn the sulphuretted hydrogen to sulphurous acid and utilize the latter in acid-chambers entirely failed; and Gossage's next proposal, to absorb the gas by ferric oxide and burn the FeS in pyrites-burners

(see below), could not be carried out. His third proposal was, to pass sulphuretted hydrogen into a solution of ferric chloride, which would thereby be converted into ferrous chloride, sulphur being precipitated; the ferrous chloride was to be reconverted into ferric chloride by the action of air; but this could not be done on the large scale with sufficient speed and completeness. This proposal, as we shall see, was afterwards taken up again more than once. The task, which has so entirely failed of accomplishment at the hands of such a fertile inventor and at the same time such an experienced practical man as Gossage was, has not been accomplished by any body else, unless this is done by Schaffner and Helbig's new process (see below), which, however, starts from a totally different principle.

For *burning sulphuretted hydrogen* a number of proposals have been made, mostly based on passing a mixture of the gas and air through a fire. In practice the difficulty of generating a uniform current of SO_2 has been found too great, chiefly owing to the sulphuretted hydrogen being much diluted with indifferent gases. A detailed description of the methods and apparatus employed for this purpose by Lee and Gossage, is found in Richardson and Watts's 'Chemical Technology,' vol. iii. pp. 15–27. Neither has E. Kopp's proposal been practically successful—viz. burning the sulphuretted hydrogen with just sufficient air for the combustion of the hydrogen only, and separating the sulphur. (*Indirectly* this has been accomplished by Schaffner and Helbig.)

It is usually asserted that one of the greatest difficulties in utilizing H_2S for making sulphuric acid is the fact that a much larger amount of inert gases must be conveyed into the chambers than when burning brimstone or even pyrites. The difference in comparison with the latter, however, is not very great. In the former case, apart from the unavoidable excess of air, each atom of sulphur requires three of oxygen and the corresponding nitrogen. In the case of pyrites 4 sulphur require 15 oxygen

$$(2\,FeS_2+15\,O+4\,H_2O=Fe_2O_3+4\,SO_4H_2)\,;$$

in that of H_2S only $\frac{1}{16}$ more is required, viz. one sulphur to four oxygen $(H_2S+4\,O=SO_4H_2)$; this sixteenth would not be of very much consequence, considering the great excess of oxygen normally present in the chambers. That in the burning of H_2S just sufficient water is produced for forming SO_4H_2, is very convenient, and

saves a great deal of steam. Neither is the difficulty mentioned by A. Rose (in Graham-Otto's 'Chemie,' ii. 2, p. 335), that the temperature in burning H_2S is too high, of any importance; the gas might be cooled, most conveniently and rationally by passing it through a Glover tower and thus utilizing its heat for the concentration and denitration of vitriol. If there were no other obstacle, it would seem that sulphuretted hydrogen should be very well applicable for vitriol-making, perhaps with a little extra nitre. But it appears that thus far no practical attempt to do this has been successful from an economical point of view; the vitriol obtained hardly pays for wages, coals, and repairs, to say nothing of leaving any margin for profit.

According to the Inspector's Report for 1877–78, p. 46, the combustion of sulphuretted hydrogen, so as to make sulphuric acid in lead chambers, was first accomplished by Mr. John Thom, of Glasgow, about 40 years ago, but was given up again.

We have seen that the difficulty of burning sulphuretted hydrogen is much greater when it is mixed with carbonic acid, as occurs in many of the proposed soda-ash processes, and regularly in the decomposition of the ammonia-water of gas-works by sulphuric acid (where, however, there need be much less dilution with nitrogen). A plan for burning the mixed gases was invented by W. Hunt, and carried out at the Frizinghall Chemical Works, near Bradford. As the H_2S is apt to be extinguished by the great amount of CO_2, it is passed into a flue in which there is a coke fire. This fire has a surface nearly on a level with the base of the flue; but a little higher, and on each side of the fire, there are openings in the flue to admit air for the combustion of the H_2S, the coke being supplied with air from below. In this way the burning gas is kept continuously lighted. The hydrogen burning at the same time with the sulphur produces much heat; to get rid of this, the gas was passed through a flue 40 feet long before entering the chamber. [Why was it not used to concentrate the vitriol?] The amount of sulphuric acid made from this gas at Frizinghall is 4 tons per week, at Mr. Spence's works at Birmingham much more. There seems to be a pretty large consumption of coke, the gases from which are clearly impediments to the process, since the condensation of the acid does not take place so readily. Dr. Smith considers that the problem of converting sulphuretted hydrogen into a useful product is solved by the above process; but this can be said only from a

sanitary point of view. *Economically* it remains a fact that the combustion of dilute H_2S in acid-chambers does not *pay*; and this explains why that process, though known in substance for many years past to every body interested in the matter, has not been employed elsewhere, although many attempts have been made in that direction.

The worst, indeed, is not the extra quantity of air required for burning the sulphuretted hydrogen itself, but the fact that, in all the processes hitherto mentioned, it is not possible to operate with *pure* H_2S. In practice it is *always* expelled by carbonic acid, as the only sufficiently cheap acid; and if cheap, it is always diluted with air. The richest gas from the most rationally constructed lime-kilns usually contains not more than 25, only exceptionally 30, per cent. by volume of CO_2; the gas from burning coke is never so rich. The other 75 per cent. is mostly nitrogen, with either a little oxygen or carbon monoxide. The carbonic acid being so much diluted, even if it could be entirely exchanged for sulphuretted hydrogen, the latter would be equally so; and this must prevent the products of its combustion from being employed in acid-chambers. Carbonic acid can be purified by Ozouf's process (absorbing dilute CO_2 in a solution of Na_2CO_3, decomposing the $NaHCO_3$ by heat, CO_2 being expelled, condensing the steam and conveying away the pure CO_2, and reemploying the solution of Na_2CO_3 after cooling); but this would probably be much too costly; and then the question would have to be solved, how *pure* H_2S is to be treated in order to burn it so as to utilize it in an acid-chamber *at a profit*. Such pure H_2S is obtained in Wallace and Claus's process, to be mentioned directly, but in too expensive a manner.

Favre (patent of June 7th, 1855) proposed introducing the sulphuretted hydrogen into pyrites-kilns, where, in contact with the burning pyrites, it is said to be burnt completely. This process is stated to have been employed in practice at Kunheim's works in Berlin upon the H_2S given off in the manufacture of ammonium sulphate. But even if the chamber process was not disturbed by this, which remains to be proved, it could not be done with such quantities of the H_2S as would be evolved in the treatment of tank-waste. The difficulty, still unsolved, is, to effect the *complete* combustion of *large quantities* of (dilute) H_2S. In order to evade the apparently hopeless attempt at direct utilization, in the acid-cham-

bers, of the SO_2 arising from the burning of H_2S, Gossage (patent of Oct. 6, 1857) proposed absorbing the sulphurous acid in water and oxidizing it by air. That he failed in this, we have seen (Vol. I. p. 650). Neither was he more successful in his proposal (contained in the same patent) to drive off the SO_2 by heating its aqueous solution to 65° and conveying the pure SO_2 gas into an acid-chamber. Wallace and Claus (patents of Jan. 20 and July 25, 1877) cause the impure sulphurous acid, obtained by burning H_2S, to act upon ammonium sulphide, which is thus converted into hyposulphite; the latter is decomposed by sulphuric acid; and the sulphurous acid, now evolved in a pure state, is employed for purifying coal-gas from sulphuretted hydrogen.

Another easily suggested mode of utilizing sulphuretted hydrogen is, by *bringing it together with sulphurous acid to produce sulphur*. Formerly it was generally assumed that in this case water and sulphur are chiefly or exclusively obtained

$$(SO_2 + 2H_2S = 2H_2O + 3S).$$

Hence it was proposed to pass the H_2S into a saturated aqueous solution of SO_2, obtained by burning pyrites or a portion of the H_2S itself. Gossage (patent February 22, 1859) constructed an apparatus for intimately mixing SO_2 and H_2S in the gaseous form. Brunfaut ('Journal des Mines,' 1861) allows the gases to act upon each other in a chamber the walls of which are wetted with water, and then passes them through a column of water before allowing them to escape. The dilution with indifferent gas is said by him, in opposition to Rosenstiehl (see below), not to interfere with the reaction. But the reaction does not proceed so smoothly as the above equation would indicate. Dalton, in 1812, had observed the formation of an acid in this process. Pelouze (1842) took it for hyposulphurous acid; but Wackenroder, 1847 (Archiv der Pharmacie, xlvii. p. 272, xlviii. p. 140), declared it to be "pentathionic acid," formed by the reaction

$$5H_2S + 5SO_2 = S_5O_6H_2 + 4H_2O + 5S,$$

which has been generally accepted since. Fordos and Gélis, in 1848, believed they had obtained that acid in another way; and several chemists made further investigations respecting it, no one doubting its existence, till Spring showed (Bull. de l'Acad. royale de Belgique, mai 1878, xlv. p. 579) that all former investigators

had mistaken tetrathionic acid for pentathionic acid, and that the latter acid does not exist at all*.

Tetrathionic acid, according to Spring, might be formed directly from H_2S and SO_2, as shown by the equation

$$4\,SO_2+3\,H_2S=S_4O_6H_2+2\,H_2O+3\,S$$

(which, however, is entirely imaginary)—or, it is much more likely, in consequence of the precipitation of sulphur, which along with sulphurous acid would form hyposulphurous acid, the latter being instantaneously decomposed by more SO_2 into hydrosulphurous acid and tetrathionic acid. The following equations show the stages of this process:—

$$\begin{aligned}&(1)\quad SO_2+2\,H_2S &&=2\,H_2O+3\,S\,;\\&(2)\quad SO_2+H_2O+S &&=S_2O_3H_2\,;\\&(3)\quad SO_2+2\,S_2O_3H_2 &&=H_2SO_2+S_4O_6H_2.\end{aligned}$$

After it had been recognized that it is impossible to precipitate all the sulphur, a good deal of it remaining dissolved in the shape of an acid (generally held to be pentathionic acid), many attempts were made to obviate this; for practically not quite half of the theoretical quantity of sulphur could be obtained, partly owing to the formation of that acid, partly on account of the extremely fine state of division in which the sulphur is precipitated, making it next to impossible to obtain a clear liquid either by subsidence or by filtration, either on a large or a small scale. Gossage believed that a high temperature of the gases at the time of their coming into contact would remedy the evil. De Luca and Ubaldini (Compt. Rend. lxiv. p. 1200) published an extensive memoir on this matter, from which, in the absence of numerical statements, not much information can be derived. Weldon (patent of Aug. 28, 1871) thought to avoid the formation of pentathionic acid by passing the sulphuretted hydrogen into a saturated solution of sulphurous acid; but this process, which is practically identical with that proposed from the first, could not attain the object. Rosenstiehl (Bull. Soc. Ind. Mulh. 1870, p. 127) stated that, the drier the gases when they meet, the less pentathionic acid is formed; when

* The paper of Stingl and Morawsky, to be quoted below, still maintains the existence of pentathionic acid; so that this question cannot yet be regarded as definitely settled. It is also maintained by Kessler, one of the first chemists who worked at pentathionic acid, that Spring has not given sufficient reasons to prove his point (Annal. der Chemie, cc. p. 206).

once the reaction has commenced, the water formed suffices for continuing it. The quantity of pentathionic acid might be kept down to a minimum, if the H_2S were in slight excess. The reaction was stated to proceed properly only when undiluted sulphuretted hydrogen was employed—that is, not formed by burning sulphur or pyrites in the air, it being then mixed with nitrogen and oxygen in excess, but, for instance, made by igniting pyrites with basic ferric sulphate, or with ferric oxide, or, best of all, by washing the SO_2 out of burner-gases in a scrubber, and heating the watery solution (which Gossage had done already in 1859). But this process would be too expensive, and the proposal must have remained sterile.

The difficulty has at length (in 1878) been overcome by the process of Schaffner and Helbig, which will be described at the end of this chapter. They have proved that all the sulphur can be obtained in a granular, easily separable form, and without any loss by polythionic acids, if the gases are brought into contact, not with water, but with solutions of such salts as calcium chloride, magnesium chloride, &c. They do not venture upon an explanation of this fact; but one might be deduced from Spring's subsequently published paper, mentioned above. According to him, the whole process is based upon the conversion of sulphurous acid into hyposulphurous acid by finely divided sulphur, which by the action of H_2S and SO_2 is certainly produced in an almost molecular state of division. Now it has often been noticed, for instance in the case of potable water, that solid substances in the state of extremely fine suspension in water are caused to aggregate and precipitate by the action of salts (such as alum &c.)—probably by arresting the "Brownian" movement of the finest particles. When once the finest particles of sulphur have been aggregated into coarser masses, the action of SO_2 upon them in the cold is very slow, and the formation of thionic acids is consequently greatly diminished. Even a subsequent addition of calcium chloride &c. to the milky liquid obtained at first suffices to clarify it. Schaffner and Helbig believed that calcium or magnesium chloride and other salts (in an additional German patent, No. 6895, of Dec. 22nd, 1878, they mention also muriatic acid, sodium sulphate, magnesium sulphate, barium chloride, sodium chloride) both prevent the formation of polythionic acid and destroy it when once formed; but Stingl and Morawsky, in an exhaustive investigation of their

process (Journal für praktische Chemie [2], xx. p. 76), proved that only from 86 to 94 per cent. of the sulphur is precipitated as such, the remainder existing, according to them, in the state of pentathionic acid, or, if the hydrates or carbonates of alkalies or alkaline earths are present, in the state of other sulphur compounds, resulting from the decomposition of pentathionic acid and sulphur, viz. sulphites, hyposulphites, and polysulphides. The formation of pentathionic acid is lessened by an excess of, and by long contact or heating with, sulphuretted hydrogen; but these conditions are just those which cannot very well be observed in practical work; and complete decomposition of that acid would take so much time as to be quite out of the question. Stingl and Morawsky further proved that the milky form of the precipitated sulphur produced by the mutual decomposition of H_2S and SO_2, has nothing to do with the pentathionic acid: the action of mineral salts and acids, in changing this milky into a denser, flocculent state is by them regarded as a merely physical one, viz. the breaking-up of microscopical hollow globules, formed by the sulphur, by the diffusion into them of those mineral substances. Possibly this explanation may hold good along with that given above by the author.

Another way of getting rid of sulphuretted hydrogen, which is suggested by the daily practice of gas-works, is to absorb it by *ferric hydroxide* (hydrated iron oxide). The iron sulphide formed, if exposed to air, regenerates the hydroxide with separation of sulphur (thus:

$$2\,FeS + 3\,O + 3\,H_2O = Fe_2(OH)_6 + 2\,S),$$

and can again be used for absorption till the sulphur has accumulated so much in it (50 or 60 per cent.) that the mass ceases to act. It can then be treated with carbon disulphide, in order to dissolve and recover the sulphur as such, or burnt, in order to convert the sulphur into sulphuric acid. As a source of iron oxide the nearest material, burnt pyrites, is not suitable, because, even after long weathering, it absorbs the H_2S too slowly. Gas-works employ some varieties of finely divided brown iron-ore, *e. g.* the bog-ore from the north of Ireland; and alkali-manufacturers would have to use something like this for their H_2S. The application of ferric hydroxide for absorbing the H_2S arising in the decomposition of tank-waste, or in that of sodium sulphide by CO_2 &c., has been very frequently proposed; and all possible apparatus have been

indicated for it. It has also been proposed (*e.g.* Wilson's patent of June 3rd, 1859) to regenerate the mass when it has become inactive in the absorbers, by conveying a current of air through it, till it is too much saturated with sulphur, and burning off the latter afterwards. Weldon patented the same, with the modification of employing the ferric oxide (*e.g.* from Fe_2Cl_6 and lime) suspended in water and alternately passing H_2S and air through it (see below). Arrot patented (June 3rd, 1859) absorbing the H_2S by red-hot Fe_2O_3 or Mn_2O_3. The author, in his patent of April 20, 1866, proposed a number of analogous absorbents, such as a mixture of milk of chalk and solution of ferrous or manganous chloride, employed in agitators with pressure, or in scrubbers without pressure; but this was not tried on a large scale. The dry purifiers, as employed by gas-works, seem to be excluded by the enormous space they would occupy in any large-sized manufactory. Spencer (provisional protection, Oct. 19th, 1859) patented the employment of ferroso-ferric oxide, obtained from burnt pyrites ignited with coal, or a similar compound of manganese.

In Gibb and Gelstharpe's patent for working up burnt pyrites (Vol. I. p. 613) the H_2S was absorbed by copper salts, and that completely, but the sulphur was not utilized in the metallurgical treatment of the copper sulphide obtained; nor has the process been successful on the whole. They (along with Hall, Nov. 21st, 1871) also patented this process generally, viz. passing H_2S into cupric sulphate bought on purpose, drying and roasting the CuS and converting it again into $CuSO_4$; but the sulphuric acid liberated in the precipitation of $CuSO_4$ by H_2S could not pay the cost of the process, which is therefore unpractical.

Wallace and Claus (July 25, 1877) again patent the employment of H_2S (obtained in their patent process, p. 346) for precipitating copper, silver, or lead from their solutions, and also for purifying sulphuric acid from arsenic. The latter process, long before in use on a large scale (comp. Vol. I. p. 469), can only dispose of a comparatively very small quantity of sulphuretted hydrogen.

Claus (March 17, 1869) and Weldon (Aug. 18, 1871) patented the absorption of H_2S by conducting the gas through a coke-tower in which a solution of a per-salt of iron, *e.g.* Fe_2Cl_6, runs down. The per-salt is converted into a proto-salt, with separation of sulphur ($Fe_2Cl_6 + H_2S = 2\,FeCl_2 + 2\,HCl + S$); air is then blown through the tower and thus the per-salt regenerated. This proposal (essen-

tially the same as that of Gossage, mentioned p. 642) was taken up again by Weldon in 1876, in connexion with his process for making soda from Na_2S. He prescribed a special, apparently very rational, apparatus for absorbing the H_2S; the recovery of the per-salt of iron was to be effected in an oxidizing-tower, exactly in the same way as in his manganese-recovery process. Since the whole soda process was abandoned again after a short trial, there are no conclusive experiences extant as to the value of that part of it which refers to the absorption of H_2S.

The only way of dealing with the H_2S, which seems to give promise of real success, is that of Schaffner and Helbig, which will be described at the close of this chapter in connexion with the process for treating tank-waste, of which it forms a part.

Other Plans for utilizing the Sulphur of Tank-waste.

Apart from the endeavours for utilizing the sulphur of tank-waste in the shape of H_2S, many attempts have been made in other ways; and success has been obtained in two respects—viz. obtaining calcium or sodium hyposulphite, and obtaining the sulphur itself. We shall first enumerate the different proposals in historical order.

The first patent taken out in this line seems to have been Leighton's (April 1836). He allowed the tank-waste to oxidize in the air for some time, lixiviated it, and precipitated the sulphur from the liquors by hydrochloric acid. In this crude way no success could be obtained.

W. S. Losh, on July 6th, 1852, patented the production of sodium hyposulphite from oxidized tank-waste. His process, as well as the other plans for obtaining that salt, will be described in the next chapter.

Delanoue (Compt. Rend. xl. p. 702) proposed boiling the tank-waste with water and sulphur, in order to convert the CaS into soluble CaS_2, and employing the solution for medicinal purposes, for protecting the vine against the *Oïdium*, for precipitating cobalt and nickel, &c.

E. Kopp published in 1858 (Bull. Soc. Industr. de Mulhouse, 1858, p. 143) a process for obtaining hyposulphites from tank-waste by the action of sulphurous acid (see next Chapter).

Spencer (patent, April 9, 1859) proposes to evolve H_2S from tank-waste by means of HCl or CO_2, absorb it by a lower oxide than

Fe_2O_3, or by pyrites or manganese partly reduced by igniting with coal, regenerate this a number of times by exposure to the air, and obtain the accumulated sulphur by distillation, or burn it to SO_2.

Townsend and Walker (patent, December 11, 1860) employ the oxidized waste for obtaining hyposulphite; they also treat the yellow sulphur-liquor by the still-liquor from chlorine-making, and indicate the principles of all other better worked-out sulphur-recovery processes; they also describe the process of oxidation of tank-waste, and the gradual formation of several products, quite correctly.

Jullion (patent, Feb. 9, 1861) takes a considerable step further: he saturates the yellow liquor with SO_2, and the resulting solution of calcium hyposulphite with HCl; he also proposes evaporating the yellow liquors with small pyrites, and burning the whole in a pyrites-burner.

Noble (patent, July 6, 1861) also describes the oxidation of yellow liquor, its treatment in a scrubber with SO_2, and the production, from the calcium hyposulphite obtained, either of sodium hyposulphite by means of carbonate, or of sulphur by adding HCl; he already prescribes adding fresh yellow liquor for saturating the resulting SO_2.

Ward (patent of September 11, 1862) ignites tank-waste with sodium sulphate, by which he intends producing a double compound of sodium and calcium which can replace soda in some cases.

Löwig (Professor at Breslau) proposed (according to an undated communication of Gundelach's to Scheurer-Kestner, in Bull. Soc. industr. de Mulhouse, Fév. 28, 1868) the treatment of tank-waste with a solution of ferrous chloride. The iron sulphide resulting is moulded into bricks and exposed to the air, in which a mixture of ferric oxide and sulphur is formed. The product is dissolved in hydrochloric acid with addition of metallic iron, in order to re-form $FeCl_2$ and obtain the sulphur as a residue.

Hewitt (patent, Feb. 20, 1877) mixes the tank-waste with silica, and heats the mixture in a furnace by a current of hot air. Calcium silicate is formed, and the sulphur is driven off in the shape of SO_2 or SO_3, which are collected and utilized in a suitable manner.

Recovery of Sulphur.

This, as we have seen, has been aimed at by a large number of patents since Leighton's; but none of the methods proposed was economically practicable. It was attained, however, nearly simultaneously (in 1861) by Schaffner and by Mond, who worked quite independently and elaborated processes differing from each other in many details. In 1866 another process was added, originally suggested by E. Kopp, but practically worked out by Buquet and especially by P. W. Hofmann, and patented by the latter. Of the English patents the earliest is that taken out by Mond (Aug. 13, 1862) for oxidizing on trays; next followed Mond's patent for oxidizing by a current of air in the lixiviating-tanks themselves (Sept. 8, 1863); then followed that of Schaffner (Sept. 23, 1865), and last that of P. W. Hofmann (Oct. 8, 1866). Mond's process is the only one carried out in England (by a small number of works only); in Germany generally Mond's and Schaffner's processes are combined; Hofmann's process is only in use at Dieuze.

It is only right to mention that Schaffner, as he has proved to the author by original letters, had sent the description of his process to England for the sake of taking out a patent, twelve months before Mond's patent, and that to a Dr. H. in Swansea (now dead). Through the mediation of the latter, negotiations were entered upon with several English manufacturers. These negotiations were proceeding favourably, but were suddenly broken off when Mond's patent came out, and when it was discovered at the same time that Dr. H. had, most unaccountably, not yet taken out a patent for Schaffner, which was then done, but too late. In this way the date of Schaffner's patent came to be later than that of Mond's.

We must also mention a claim of priority in respect of the process known as Mond's, on behalf of Dr. Guckelberger, of Ringkuhl near Cassel (Jahresb. f. Chemie, 1868, p. 926; Wagner's Jahresb. 1870, p. 164; Dingler's Journal, ccii. p. 266; cciii. p. 473). In Germany that process is often mentioned as Guckelberger's; and Mond is only mentioned secondarily, as having improved the process in a few details. This does not appear to be justified by the documents published. No doubt Guckelberger had made experiments for utilizing the sulphur of tank-waste even before Mond, and he had induced Mond to make further experi-

ments on this subject under his direction in 1859–61. But it is not disputed at all that these experiments did not yield a satisfactory result, any more than those made independently by Guckelberger after Mond had left him, whilst Mond on his part by independent experiments and a large number of trials on the large scale, at Utrecht and Widnes, worked out his process, which was patented in 1863 (not to mention his first patent, of 1862, for oxidizing in thin layers). Guckelberger himself, in a certificate published by Mond, dating from 1862, speaks of "Mond's process" as a successful one, and thus acknowledges the experiments made under his direction as Mond's mental property. Not till 1864 did Guckelberger himself make regenerated sulphur on a large scale, which had been done by Schaffner in an impure state in 1860, in a pure state ever since 1862, as well as by Mond in the same year. Although we must not overlook the fact that Guckelberger worked on this subject before Mond, and that he had some good ideas about it, yet he can only be mentioned along with the above-named English inventors, Townsend and Walker, Jullion, and Noble, whose proposals were not practically successful, whilst Mond, and not Guckelberger, appears along with Schaffner and Hofmann as the inventor of a process practically successful on the large scale. Nobody seems to work by Guckelberger's process, as far as it essentially deviates from Mond's; but Mond's process is used at all English works at which sulphur is recovered.

Schaffner's Process,

as may be seen from his own report (Dingl. Journ. cxciii. p. 42), was quite gradually developed. About the year 1859 he had conceived the idea of making sodium hyposulphite from tank-waste (as some English inventors had done previously), upon noticing, on hot summer days, that salt as an efflorescence on tank-heaps, which reappeared after the salt had been scraped off, and seemed to show that its collection and purification would be a paying process. In order to remove a small quantity of sulphides, he added a little hydrochloric acid, because he had found that this acted upon the sulphides sooner than upon the hyposulphite. When, with a rising demand, the mass itself was lixiviated and hydrochloric acid added to it, much greater quantities of polysulphides were found in it, leading to a copious evolution of sulphu-

retted hydrogen and precipitation of sulphur. This suggested to Schaffner the idea of making the sulphur the principal thing, and studying the best conditions for its recovery. Very soon he discovered the fact, of the greatest importance for that recovery, that the waste after lixiviation furnished good liquors by another oxidation and lixiviation, and that this process can be repeated several times. The first oxidation he always carried out in the heaps; the second and third, first in pits, in order to keep the heat better together, but afterwards in the tanks for lixiviating the first product with the assistance of warm chimney-gases, which takes only six or eight hours. Thus space and labour is saved, but liquors are obtained less rich in polysulphides than those made at the ordinary temperature, and hence yielding rather less sulphur.

On decomposing the liquors by hydrochloric acid, very much H_2S was given off, which caused extremely great annoyance to the workmen and the neighbourhood, and in which a considerable quantity of sulphur was lost. This suggested to Schaffner the invention of his peculiar closed sulphur-precipitating apparatus, which will be described below.

Schaffner's process in its details, as carried on at his works at Aussig, is as follows :—The first operation is *the oxidation of the tank-waste* and the *preparation of the sulphur-liquors*. The waste is taken out of the black-ash lixiviating-tanks in a damp state and cast over a wall ten or twelve feet high, running along the factory in the open air, with a tramway running parallel to it. Against this wall the waste lies, with its natural slope, in large heaps. By the action of the air, and the oxidation of calcium sulphide caused thereby, the heap gets hot after a little while. First chiefly polysulphides, afterwards more hyposulphite is formed. It is a matter of experience to judge of the duration of this first stage; a practical test for judging whether a heap is "ripe" is the greenish-yellow colour of its interior. This stage is usually reached in about three weeks; during this time the mass is allowed to lie quietly without turning. But when it is "ripe" it is hacked up, the large pieces are broken up, and the whole allowed to lie another twenty-four hours for better oxidation before it is *lixiviated*. Since in the meantime the rain-water has caused a partial involuntary lixiviation, the ground is made to slope towards a deep pit, in which the drainage collects and is pumped up from

time to time in order to serve in the place of fresh water for lixiviating the oxidized mass. This itself is done in iron tanks, quite similar to black-ash tanks, connected by overflow-pipes, so that always three of them work together and only strong liquors are obtained. There are many such sets built, each in a long row parallel with the above-mentioned wall, and the oxidizing-heaps at such a low level that the mass can be tipped directly onto them. The liquors here obtained are worked up as we shall see; the insoluble residue is oxidized again. Formerly this was done in pits, made alongside the lixiviating-tanks; and as the heat was well kept together here, the oxidation took place much more quickly than the first time. But the constant removal of the mass back into the tanks &c. cost much labour. Schaffner consequently, as Mond had already done before him, substituted carrying on the later oxidation in the lixiviating-tanks themselves, all of which are connected by branches with a fan-blast for blowing in a current of air. In order to further the oxidation, Schaffner during the cold season does not employ atmospheric air, but warm (but not too hot) chimney-gas, the CO_2 of which also assists the process. After eight or ten hours' blowing the oxidation proceeds no further; the blowing is now stopped, the mass again lixiviated, and the residue again oxidized by blowing; and this process of alternate oxidizing and lixiviating is repeated altogether six times. In all these six oxidations only one third of the recoverable sulphur is obtained; two thirds are obtained in the first oxidation in heaps. The reason is that during the spontaneous slow oxidation more polysulphides are formed, but during the forced oxidation more hyposulphite, along with more sulphite and sulphate, the sulphur of which is entirely lost. For this reason Schaffner prefers not oxidizing the waste from the first in the soda-lixiviating tanks, because much less sulphur is obtained than by lixiviating in the open air—but especially also in order not to complicate the lixiviation of soda, and to remove any danger of contaminating the soda-liquors with sulphur-liquors. Besides, only few works can spare the room for increasing the number of their lixiviating-tanks so as to make them suffice not only for the lixiviation of the black ash, but also for six or seven oxidations and lixiviations of the waste; they will prefer casting the waste once for all upon a heap outside and allowing it to oxidize slowly (which involves no manual labour), and then carrying on its lixiviations and further oxidation in sepa-

rate tanks, likewise in the open air, where space is not so much an object.

The *residue* ultimately remaining is quite harmless, and is used, for instance, by railway companies in lieu of ballast on their lines. A comparatively small portion of it is, as mentioned, employed in the soda mixture in the place of lime. After all, there is not as yet any proper use for this residue, which chiefly consists of calcium carbonate and sulphate, always with a little sulphite, along with a little ferric oxide, sand, clay, and coal. In any case it might be used as an addition to lime, in the manner described in Vol. I. p. 264, for the purpose of making a firm and very cheap hydraulic mortar. But many attempts have been made (similar to those mentioned for fresh waste) to manufacture from this residue, by burning, a real cement, which, analogous to Scott's selenitic mortar, is to replace Portland cement; and although this problem cannot be said to be solved completely, it deserves more attention than it has hitherto received.

According to communications on the part of Mr. Mond (whose residues are quite analogous to Schaffner's) the residue, desulphurized as completely as possible, is to be mixed with a quarter of its weight of coal-ashes, which contain chiefly aluminium silicate and a little coke; the mixture is charged into a kiln, damp as it comes from the tanks, in alternate layers with fuel, and burnt. A little H_2S is given off on charging, but no gas whatever in burning. A kiln with a separate fireplace, best of all with gaseous fuel, would be preferable. In this operation no doubt a mixture of CaO and $CaSO_4$ will be obtained—that is, a product very similar to Scott's selenitic mortar. Indeed, by grinding the burnt mass a very good cement is obtained, which completely sets in about eight days and has a considerable degree of hardness; a cube of 1½-inch side made of this material can bear a weight of 2 cwt. without being crushed. It is very useful for foundations in damp ground, artificial stones, &c. One drawback is the considerable efflorescence of sodium sulphate exhibited by this cement, which only ceases after several washings by the rain.

Schaffner (according to direct information received from him) made many similar trials and obtained an excellent cement; but he gave up any further trials when a small temple, consisting of very thin columns made from this material, after having stood very well for some time, suddenly fell to powder. He ascribes this to the

oxidation of calcium sulphite to sulphate, which makes it expand and loosens the mass. His trial was purposely made under the most difficult conditions; and when the cement is employed only as mortar no great inconveniences need be apprehended.

The *oxidation-processes of tank-waste* (comp. also Chapter VII.) are different according to the mechanical state and moisture of the waste, its volume, the temperature, the greater or lesser speed (that is, whether caused by the spontaneous action of the air or by a current of compressed air), and especially according to whether along with the oxygen carbonic acid (from chimney-gases) also acts upon it. In the oxidation in large heaps, by the gradual action of the air only, Schaffner distinguishes the following processes:—

(1) $2\,CaS + O = CaO + CaS_2$; later on,

(2) $CaS_2 + 3O = CaS_2O_3$; still later,

(3) $CaS_2O_3 = CaSO_3 + S$; at last,

(4) $CaSO_3 + O = CaSO_4$.

Reactions (3) and (4) lead to a loss, since both neutral calcium sulphite and the sulphate are almost insoluble. The sulphur first separated is again dissolved on lixiviation, if concentrated liquors are made, since polysulphides up to CaS_5 can be formed.

If CO_2 also acts, as on blowing with chimney-gases, the following reactions may take place:—

(5) $CaS + CO_2 + O = CaCO_3 + S$.

This takes place especially when the moisture is insufficient; the normal reactions are:—

(6) $CaS + CO_2 + H_2O = CaCO_3 + H_2S$;

(7) $CaS + H_2S = Ca(SH)_2$; or, in one equation,

(8) $2(CaS + CaO) + H_2O + 3\,CO_2 = 3\,CaCO_3 + Ca(SH)_2$.

When the chimney-gases act further, their oxygen leads to reactions (2), (3), and (4); or the following may happen besides:—

(9) $2\,CaS + 4O + CO_2 = CaS_2O_3 + CaCO_3$;

(10) $CaS_5 + 3\,O = CaS_2O_3 + 3\,S$;

(11) $CaSO_3 + S = CaS_2O_3$ (only slowly).

Lastly, even free sulphur can be formed from sulphuretted hydrogen

(12) $H_2S + O = H_2O + S$.

The free sulphur is used up on lixiviation for the formation of polysulphides and, to a smaller extent, of hyposulphites.

Kraushaar (Dingl. Journ. ccxxvi. p. 412) arrived at somewhat different results by an investigation of the decomposition of soda-waste. He found that chiefly calcium sulphhydrate, $Ca(SH)_2$, is formed in the interior of a heap, probably by a simple decomposition of calcium sulphide and water: $CaS + H_2O = Ca(SH)_2$. This reaction should be assisted by keeping the surface of the heap very smooth and avoiding cracks through which the air can enter into its interior. In this way much more of the sulphur of the waste is dissolved. Only later on should the air act; and then at first polysulphides will be formed—

$$Ca(SH)_2 + O = CaS_2 + H_2O,—$$

afterwards also hyposulphite, either by the reaction

$$Ca(SH)_2 + 4O = CaS_2O_3 + H_2O,$$

or, more probably, by this—

$$CaS_2 + 3O = CaS_2O_3.$$

In fact, during the oxidation-process the quantity of calcium polysulphide decreases and that of hyposulphite rapidly increases. If, however, the oxidation is carried on too quickly, calcium hyposulphite, together with very little polysulphide and no sulphhydrate at all, is formed. [This must be doubted so long as it is not explained why the latter compounds are formed nearly as copiously in Mond's process, where air is blown in from the very first, the whole process is finished in a few hours, and no time is given for the hydration of the lime as demanded by Kraushaar.] The total soluble sulphur, according to Kraushaar's experiments, decreases during the later stages of the oxidizing-process [of course after reaching a certain maximum], in consequence of the further oxidation of calcium hyposulphite to sulphite and sulphate. But he asserts that 90 per cent. of the total sulphur of tank-waste can be brought into solution as calcium sulphhydrate, if it is mixed with a little water and exposed to the action of steam at a pressure of 5 atmospheres in an iron vessel provided with an agitator. The calcium sulphhydrate might be employed in tanning (comp. Dingl. Journ. ccxviii. p. 355), or might be worked for sulphur in this way:—Treat the tank-waste with steam at 5 atmospheres' pressure and then filter

it; spread out in thin layers the slimy substance left on the filter; after 24 hours it will be sufficiently dry to be broken up with a shovel, will exhibit at its surface the greenish yellow colour characteristic of oxidized tank-waste, become heated, and the $Ca(SH)_2$ be transformed into CaS_2 and CaS_2O_3. The liquor containing much of the latter is to be mixed with the previously obtained solution of $Ca(SH)_2$ in such proportion that the three sulphur compounds are present in the proper ratio for precipitation by HCl. The increased cost for steam can be more than made up for by the smaller amount of labour [?], and especially by the larger yield. It does not appear that Kraushaar, even in laboratory experiments, actually obtained more sulphur *as such* than with the ordinary process; on the contrary, in trials made by Schaffner at Aussig (communicated by him to the author) only a small portion of the sulphur was dissolved by steam at 5 atmospheres' pressure; and the $Ca(SH)_2$ seems to be decomposed again by the high temperature, since on relaxing the pressure H_2S escaped in quantity. In no case could any thing like 90 per cent. of the sulphur be obtained; and the process altogether does not seem to be practicable, owing to the higher wages &c. required.

Kraushaar's process has also been tried by Mr. Curphey, assistant to Dr. R. A. Smith, with very much better results (Inspectors' Report for 1877–78, pp. 15 & 35). Soda-waste heated with water in a digester to 104° or 105° C. gave a slightly yellow solution containing 13·44 grams of sulphur per litre. After heating it five hours to 155° C. with water and washing, the sulphur of the sulphides in the waste had diminished from 8·43 per cent. to 1·18 per cent.; *i.e.* 86 per cent. had been extracted. By treating it three hours at 160° C. 82·4 per cent., by treating it 34 hours at 164° C. 87·6 per cent., by treating it five hours at 140° C. 88·9 per cent. of the sulphur was extracted. These results are encouraging enough, and point to further investigation in that direction: but Dr. Smith thinks the treatment of soda-waste under pressure too expensive; and the author agrees with him.

The *yellow sulphur-liquors* obtained on lixiviation chiefly contain calcium polysulphides, sulphhydrate, hyposulphite, and a little of the corresponding sodium salts, according to the percentage of sodium in the waste. In the beginning more of the compounds free from oxygen, later on more of the hyposulphites is formed: the proportion indicated by Mond is the most favourable, viz.

2 molecules of the compounds giving off H_2S to one molecule of hyposulphite. In any case all the liquors are run into a common tank and subjected together to the following operation.

An analysis of the Aussig sulphur-liquor (spec. grav. 1·065), made by Salathe in the author's laboratory, yielded the following composition in grams per litre.—

			Equivalent of base.
5·440	grams sulphur as sulphhydrate, corresponding to		1·70
8·208	" "	sulphide "	5·13
1·653	" "	sulphate "	1·03
16·064	" "	hyposulphite "	5·02
31·365			12·88

17·946	" " polysulphide.		
25·430	" lime (CaO), corresponding to	9·08	equivalents of S.
12·896	" soda "	4·16	" "
		13·24	

(We shall revert to the formation and composition of the sulphur-liquors later on, when describing Stahlschmidt's researches.)

The decomposition of sulphur-liquors by hydrochloric acid has been effected by Schaffner upon a very ingenious principle, realized by a peculiar apparatus, and founded upon the following facts:— Hyposulphites are decomposed by hydrochloric acid with evolution of sulphurous acid and precipitation of sulphur, thus:—

$$CaS_2O_3 + 2HCl = CaCl_2 + SO_2 + S + H_2O.$$

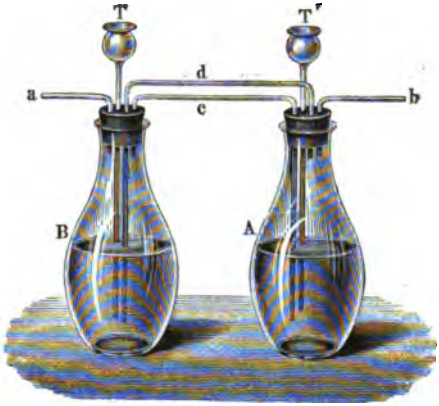
Besides, by SO_2 the soluble calcium sulphides, whether $CaSH_2$ or polysulphides, are converted into hyposulphite:

$$2CaS_5 + 3SO_2 = 2CaS_2O_3 + 9S.$$

The way in which these reactions are utilized is best shown in the small apparatus represented in fig. 254. The two flasks B and A are filled with sulphur-liquors. The tube *a* is closed by a plug and HCl poured through the funnel-tube T into the flask B. The HCl will act first upon the polysulphide and sulphhydrate, before the hyposulphite is decomposed; consequently at first only H_2S is given off, which in the beginning of the operation is allowed to escape into the air: it must first pass through *c* into the flask A, and escapes out of this through *b*. Besides, of course, the sulphur in excess is precipitated as such:

$$CaS_5 + 2HCl = CaCl_2 + H_2S + 4S.$$

Fig. 254.



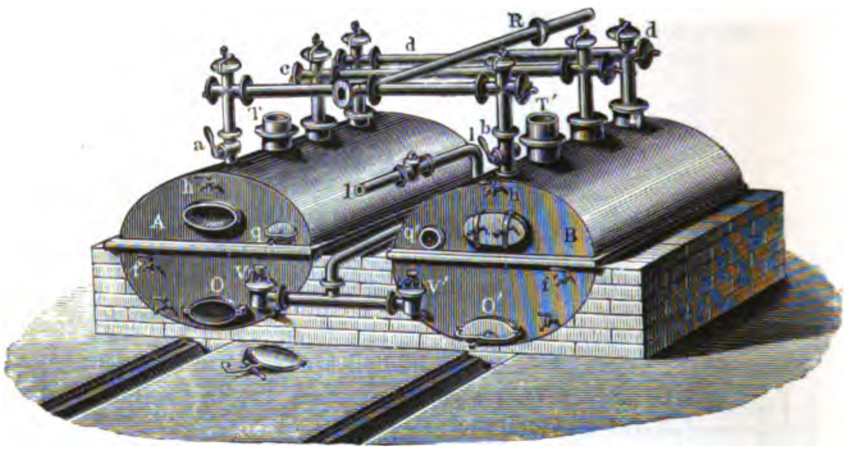
When all the polysulphide and sulphhydrate has been decomposed, a further addition of HCl also decomposes the hyposulphite, S being precipitated and SO_2 becoming free:

$$CaS_2O_3 + 2HCl = CaCl_2 + SO_2 + S + H_2O.$$

The SO_2 likewise passes over into flask A, but is absorbed there, since according to the former equations the polysulphide is transformed into hyposulphite. When the decomposition is complete, the flask B is heated to expel all the SO_2, after which it should only contain a solution of $CaCl_2$ and precipitated sulphur. It is emptied, the sulphur collected, and the flask again charged with sulphur-liquor. Now the tube *b* is closed, *a* is opened and through T' hydrochloric acid is poured into the flask A. Since in this all the polysulphide is converted into hyposulphite, no more H_2S is given off, but at once SO_2, which passes into the sulphur-liquor in B and is absorbed there, again transforming its polysulphide into hyposulphite. When the decomposition in A is finished, the sulphur is again collected, the $CaCl_2$ solution is run away, and the flasks charged with fresh sulphur-liquor. Thus the play constantly changes between B and A; and with liquor of the proper composition no gas whatever escapes, except at the start; and even then it can be avoided by charging the flask B the first time with a solution of hyposulphite in lieu of sulphur-liquor.

On the large scale the precipitation-apparatus is of cast-iron, and is represented in fig. 255. The letters here signify the same parts as in the laboratory apparatus fig. 254. A and B denote the

Fig. 255.



precipitating-vessels; *l* is the liquor-pipe, from which the liquor is conveyed by an elastic tube now to one and now to the other vessel through the openings *q* and *q′*. T and T′ are earthenware pipes for pouring in hydrochloric acid. The pipe *c* is fixed on the top of A, whilst its other limb ends nearly at the bottom of B; on the other hand, the short limb of *d* sits on the top of B, and its long limb dips nearly to the bottom of A. When the gas is to travel by *c* from A to B, the cock *a* is closed; when it has to travel from B to A by *d*, *a* is opened and *b* is closed. Any excess of gas escapes through R. After all the acid has been run in, and *all hyposulphite has been decomposed* (this should be attended to, as we shall see when treating of Mond's and Stahlschmidt's objections), steam is admitted by the valve V or V′ in order to expel the SO_2 dissolved in the liquor; then the plug in the man-hole O or O′ is opened, so that the calcium chloride solution nearly all runs away, together with the precipitated sulphur, and is conveyed to the filter by the shoot *g* or *g′*. The pet cocks *h* or *h′* serve for judging by the smell whether all SO_2 has been driven over. The cocks *f f′* serve for judging of the proper filling with the liquor and of the

progress of the decomposition. All the pipes have cleaning-flanges in their elbows. The work is carried on exactly as described with the laboratory apparatus.

The sulphur is precipitated in two forms—viz. from the hyposulphite, on adding HCl, in a semifluid form, and from the polysulphides, by SO_2, in a finely divided state. The two modifications unite to form dense finely-grained sulphur, which settles down rapidly and is easily filtered. It is separated from the calcium-chloride solution by a tank with a false bottom, upon which the sulphur remains behind and is washed with water before being sent to the melting-apparatus. It is not yet in a pure state, but mixed with gypsum, often in large quantity, owing to the sulphuric acid contained in the muriatic acid, but, with proper working according to Schaffner's prescription, *not* from polythionic acids, which certainly may be formed by secondary reactions, but under conditions deviating from the rules laid down by Schaffner, especially at a higher temperature and with longer contact of SO_2 with undecomposed polysulphide.

For works where hydrochloric acid is valuable, but where acid still-liquors from the old chlorine-process are available, Schaffner proposes a plan for utilizing the latter which partly coincides with Hofmann's process (see below). The still-liquor, which, along with much free acid and $MnCl_2$, also contains some Fe_2Cl_6, must first be deprived of the latter. This is done by adding a little sulphur-liquor; the H_2S given off at once reduces the Fe_2Cl_6 to $FeCl_2$, precipitating sulphur of a dirty colour and only fit for burning. If the Fe_2Cl_6 were not reduced first, it would be so in the precipitation-apparatus by the SO_2, with formation of $CaSO_4$, thus causing a loss of sulphur. The still-liquor can now be used in the precipitation-apparatus, its free acid acting like so much pure HCl. But if along with the hyposulphite any CaS is present, HCl must first be added, to decompose this, before still-liquor is employed.

Schaffner's sulphur-precipitation apparatus has been successfully employed for many years in manufacturing-practice. The objection has been raised (especially by Mond, Chem. News, xviii. 159) that it causes a loss of sulphur by the formation of calcium trithionate, which decomposes into S, SO, and *gypsum*; but Schaffner denies this, on the strength of his experiments and of the fact that with his process more sulphur is obtained than by direct decom-

position of the sulphur-liquors. This arises from the fact that Schaffner's apparatus permits the oxidation to be conducted in such a manner that as many polysulphides as possible are formed, which are all converted into hyposulphites by SO_2, whilst on direct precipitation in an ordinary agitator the hyposulphite ought to be in slight excess, and the oxidized residue then contains more insoluble calcium sulphite and sulphate. Mond, who always speaks of the decomposition of hyposulphite by hydrochloric acid at a boiling heat, has overlooked that Schaffner operates without heating, and only at the end admits steam for driving off the SO_2. Mond asserts, according to his theory, that in Schaffner's process only liquors rich in hyposulphites can be employed, because otherwise hardly any SO_2 is liberated; whilst, inversely, Schaffner points out as an advantage of his process that the oxidation can be so conducted as to obtain liquors rich in polysulphides and poor in hyposulphite. This contradiction can probably be explained by the fact that Mond and Schaffner worked at different temperatures. The same holds good of the research of Stahlschmidt to be mentioned below, which, for the same reason as Mond's, is not conclusive as to Schaffner's process.

Experiments made by the author have entirely corroborated Schaffner's statements. In working with the glass apparatus, fig. 254, SO_2 was admitted until all the polysulphides had been converted into hyposulphite and the liquor had been decolorized with a strong precipitation of sulphur (even a small excess of SO_2 does no harm); if then an excess of HCl was added without heating, and a little time allowed to pass before heat was applied, on the latter taking place streams of SO_2 were given off, and the precipitated sulphur, after filtering and washing till the end of the acid reaction, left no residue whatever on burning. Hence no calcium sulphate, and previously no trithionate, had been formed. An exact description of the author's experiments made for refuting Mond's and Stahlschmidt's sulphur-precipitation theory has been published in 'Dingler's Journal,' ccxxviii. p. 252.

The sulphur precipitated in Schaffner's apparatus appears in a granular form, very convenient for washing; nor does it give out such a disagreeable odour as that precipitated in Mond's agitator. In the latter the sulphur-liquor runs into an acid liquid; this causes the formation of hydrogen persulphide, which adheres to the sulphur as a stinking oily fluid, and cannot be entirely driven

off by melting with steam; only the method of purification introduced by Schaffner, blowing air through the melted sulphur, can remove the unpleasant smell.

Schaffner, in spite of these advantages of his apparatus, has recently, like Mond, adopted precipitation in an agitating vessel, because this kind of work is simpler and better adapted for working on a very large scale, the saving in wages and repairs makes up for the smaller yield of sulphur, and the smell can be removed as just mentioned.

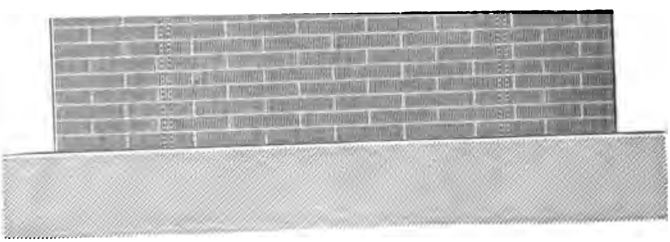
The purification of the precipitated sulphur from the calcium sulphate has been effected by Schaffner by a peculiar method, which, owing to its great suitability for the purpose, has been almost universally adopted. By it as good as chemically pure sulphur is obtained, which is regularly sold as refined brimstone. It is not at all easy to purify the sulphur precipitated in the wet way by melting or distillation; the sulphur is so light and porous, and, in consequence of the admixture of gypsum, such a bad conductor of heat that the sides of the melting-pans may be at a white heat whilst the sulphur in the centre is scarcely warm. Schaffner discovered by accident that the sulphur can be purified by melting it in a concentrated solution of calcium hyposulphite or chloride, the boiling-point of which is above the melting-point of sulphur; but this process is a little costly and uncleanly. He ultimately found that the difficulty was entirely overcome by melting the sulphur in a closed vessel *under water at a pressnre of* 1¾ *atmosphere* above that of the outer air, so that a temperature exceeding the melting-point of sulphur (111·5° C.) is attained. In this way not merely is the calcium chloride adhering to the sulphur dissolved in the water, but the gypsum is suspended in it as fine crystals, while the melted sulphur is collected at the deepest part of the pan, whence it can be run off and cast into moulds. Only after the sulphur, and sharply separated from it, does the water, together with the gypsum suspended in it, run away. At the same time with the sulphur a little milk of lime is put into the apparatus, in order both to neutralize any free acid and protect the metal from it, and to remove any arsenic. The lime with the sulphur forms calcium sulphide, which combines with the arsenic sulphide to form soluble calcium sulpharseniate; and this passes over into the water. Melting under water consequently affords many advantages. The precipitated sulphur need not be washed very much, and need not

be dried at all; it is made free from arsenic and obtained at once in the refined state without distillation. It is also an advantage for casting in moulds, that by melting the sulphur in this way it cannot be heated beyond the point at which it forms a thin liquid.

Melting by water under steam pressure has been carried out in a variety of apparatus, especially in England, mostly in order to avoid employing the apparatus patented by Schaffner. But the latter's own apparatus has proved the best, and is employed by most works. It is shown in fig. 256 with all its details, from a large drawing which the author owes to the kindness of Mr. Schaffner. An inner cast-iron cylinder is surrounded by an outer wrought-iron one; the former has no ends, but on both sides reaches up to the ends of the latter, and is flanged to them. The whole is inclined to one side, so that the sulphur can collect in the lowest part. The sulphur from the filters, mixed with a little milk of lime, is introduced in the state of mud into the inner cylinder through the man-hole M of the outer cylinder, and an open pipe joined to the same. The steam enters through the valve V into the annular space between the cylinders, and then through the open branch *o* into the inner cylinder; by an agitator, whose shaft passes by glands through the two ends and is turned round by means of the pulley R, driven by an engine, the steam is whipped up with the mud of sulphur and water and the heat equally distributed. X are turned collars slipped on the agitating-shaft, which can be easily renewed when worn out; V′ is a valve for running off the condensed water; V″ another, for blowing off the steam at the end of the operation; S, a rod with a tapering plug for tapping the sulphur; P, a removable shoot for preventing the sulphur from being squirted about in running off; T, a vessel for receiving the melted sulphur. The dome C is provided because on blowing off the steam through V″ the inner liquid boils up violently, and without the dome it would be projected into the outer cylinder.

The yield of melted sulphur at the Aussig works amounts to 14 parts for each 100 parts of pure sodium carbonate (in the shape of soda ash).

The sulphur melted by Schaffner's apparatus was from the first practically as pure as refined brimstone; but it could not at first easily compete with the latter, because its colour was rather darker,



[illegible]

[illegible]

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owing to traces of organic substances, because it had the abovementioned disagreeable smell of hydrogen persulphide (discovered in it by A. W. Hofmann, Deutsch. chem. Ges. Ber. i. p. 82), and because it was more bulky than Sicilian brimstone. The colour could soon be improved by increased cleanliness in manipulating; but the bad smell could not be easily got rid of. Schaffner at last succeeded in doing this by the following process:—The sulphur is melted up again in a cast-iron pot, and a strong current of air blown through it by a blowing-engine for some hours. Thus not merely is all hydrogen persulphide removed, but also any mechanically enclosed water; moreover, at the bottom of the melting-pot a little black FeS is found, which would otherwise give to the sulphur a greenish tinge; the latter thus becomes more purely yellow. It was the enclosed water that made the recovered sulphur more porous and consequently specifically lighter, exciting the prejudice of match-makers against it. After this treatment it is cast in moulds, and cannot be distinguished by its colour, density, &c. from refined Sicilian brimstone.

There were made by Schaffner's process in 1872:—at Aussig 500 tons of sulphur along with 2000 tons of hyposulphite of soda; at Stolberg (by a combination with Mond's process) 285 tons, at Griesheim 200 tons, at Heufeld 115 tons, at Heinrichshall and Lüneburg 100 tons each.

Mond's Process.

In no quarter is it disputed that the experiments of Mond, who at that time was chemist at the Ringkuhl works near Cassel, were suggested, in 1860, by Guckelberger, the manager of the works. But it is nowhere asserted that Guckelberger had previously made any original discovery—except by Tiemann, in Hofmann's 'Bericht,' i. p. 480, according to whom Guckelberger, like Schaffner, had noticed the tendency of tank-waste to yield several liquors by repeated oxidation (which Mond claims to have done himself, in Chem. News. xviii. p. 157),—or that his experiments and those made by Mond under his direction had led to any practically available result. Hence Mond cannot be denied the full merit of having, after leaving Ringkuhl, by independent researches and entirely novel ideas discovered a practically available and economically successful process. His experiments were from the first directed

towards hastening the slow process of oxidation. He first attempted (Tiemann, *l. c.* p. 480) to hasten the oxidation by exposing the waste, in casks with perforated false bottoms, each carrying a chimney, to an ascending current of air—but not with the desired success, as the spongy state of the waste interfered with the entrance of the air. He further tried spreading the waste in thin layers on trays and exposing it to the air. This process he patented in France in 1861, and practically carried it out at Utrecht. It took, however, too much time, space, and labour to be available for large works, as Mond saw most clearly when, in 1861, he came to England. He found here tank-waste obtained by Buff-Dunlop's lixiviating process, and consequently much more open than that obtained by Clément's process, to which he had been accustomed. This induced him to return to his first idea, of oxidizing the waste by an artificial current of air. This time his experiments were crowned with success—in the first place, because the waste was more suitable for it, and, secondly, he produced a much more energetic current of air by means of a Schiele's fan-blast. The English patent for this process is dated from Sept. 8th, 1863. The most important communications on his process are contained in the Chem. News, xvi. pp. 27 & 41, xviii. p. 157, and in a pamphlet on the Recovery of Sulphur from Alkali-waste (1869) *.

The description given in the following is chiefly based on the practical working of the process as arranged by the author under Mond's direction, and carried out for a number of years.

The most striking difference between the process of Mond on the one hand, and those of Schaffner and Hofmann on the other, is this—that in the former the tank-waste remains in the black-ash tanks and is oxidized in these, and that it is only cast out after being desulphurized, thus permitting a more continuous operation than oxidizing in heaps. The number of tanks for this purpose must be increased in the ratio of 4 : 10; it is better to increase them even in a little ampler proportion. Moreover the tanks must be provided with some special contrivances for this object. They

* One of Mr. Mond's workmen at Widnes, B. Jones, on May 25th, 1864, took out a patent for an "improvement," which did not, however, turn out successful. It consisted in blowing steam into the waste till its temperature got up to 93° C., then lixiviating with water and steam, again exposing to steam and air, and so forth.

have now three functions to perform in succession :—1st, the ordinary lixiviation of black ash; 2nd, the oxidation of the waste; 3rd, the lixiviation of the sulphur-liquor. The functions 2 and 3 must be carried out alternately at least three times, better four times, or even more frequently.

In the first place, the tanks must be so arranged that the liquor contained in them can be *completely* run off; any sulphur-liquor remaining in them would give the greatest possible trouble in the next following black-ash lixiviation. Unless the tank-bottoms are from the first inclined to one side and the cocks so placed that the whole of the liquor can be run off, a sloping false bottom of bricks set in cement must be put, to effect the same purpose. The whole tank must be thoroughly cleansed every time, after finishing the lixiviation of sulphur-liquor, by a strong jet of water and brushing out all the corners. This is somewhat troublesome; and the complete cleaning of the tanks cannot be depended upon, as is soon shown by the quality of the ash. Hence some factories entirely separate the black-ash lixiviation from the sulphur-recovery, by arranging the black-ash tanks above those for the sulphur-recovery process, and providing the bottom of the former with a trap door, accessible from below and closing watertight, corresponding with one of the movable sieve plates above. After finishing the soda-lixiviation and running off the water, the bottom trap is opened, the sieve plate above it removed, and the waste shovelled down into the sulphur-tanks. In this case the soda-tanks are made as usual; but where all the tanks are at a level, all of them must be provided both with the ordinary fittings of black-ash tanks and with those peculiar to the recovery-tanks. These latter are a contrivance for blowing in air and another for washing out the sulphur-liquor. For generating the current of air a Schiele's noiseless fan-blast is employed, as shown in figs. 257 and 258, from two sides. Such a fan of 2 feet diameter suffices for smaller works, one of 3 ft. for the largest works; the moving power required is only 1 or 2 horsepower. The highest necessary pressure is 4 inches water; but 1 inch is mostly sufficient. From the fan-blast an 8-inch pipe of galvanized sheet iron passes high above the tanks, so as not to interfere with the work in them, and sends a 4-inch branch into each of them. The portions of the air-pipes in the tanks themselves must be made of cast iron, in order to stand the pressure of the mass and the rough touches of shovels; these cast-iron pipes

Fig. 257.

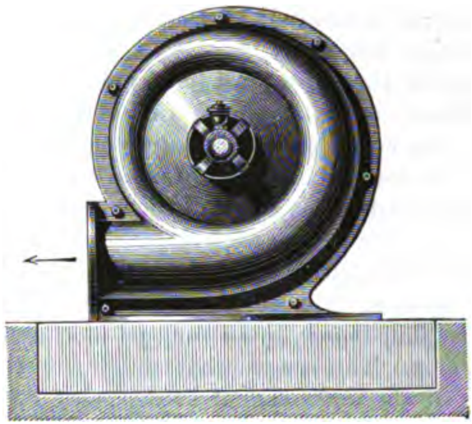
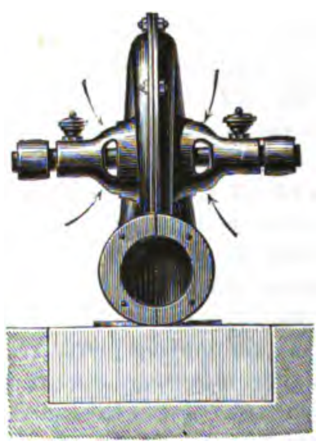


Fig. 258.



carry on their top the simple shut-off valves shown in figs. 259 and 260; as a small loss of air is of no moment, nothing more expen-

Fig. 259.

Fig. 260.

sive is needed. Such a valve is a box-like expansion of the pipe, in which a small cast-iron slide is put in more or less, to regulate the access of the air or shut it off altogether. Experience has shown that the air-pipe need not have any branches below the double bottom; and the latter itself is a sufficient distributing-apparatus.

In order to judge how far the slide is to be opened each time, the differential ether-anemometer, described in Vol. I. p. 331, is employed. First it is found out once for all for each tank what pressure the instrument shows for proper oxidation; and the later operations are regulated accordingly. In order to apply the anemometer, a 1-inch hole, usually closed by a plug, is made in the air-pipe.

The progress of the oxidation is moreover tested by outward appearance. The mass becomes hot (up to 90°); steam issues from it; and first green, then yellow spots appear, which ultimately cover the whole surface; and at last the mass becomes quite dry. If the blowing were continued too long, it would become red-hot. A very faint smell of H_2S is frequently noticed. The duration of the operation is partly determined by these tests, partly by the experience to be gained individually at every works, as to the kind of work by which the proper proportion between sulphides and hyposulphite is attained. Usually from 14 to 16 hours suffice for fully developing the action of the air; by longer blowing no more sulphur becomes soluble, since then only hyposulphite, sulphite, and sulphate are formed.

The fittings for *lixiviating* the soluble sulphur compounds formed, if there are separate tanks for the sulphur-recovery, are quite similar to those of black-ash tanks. But if both the black-ash work and the sulphur-recovery are carried on in the same set of tanks, the lixiviation belonging to the sulphur-recovery is carried out by running off the liquor through the bottom-cock and pumping it up into another tank. For this purpose three shoots run along the tanks underneath the bottom-cocks, leading into as many store wells; one of them serves for weak soda-liquor, another for weak sulphur-liquor, the third for strong sulphur-liquor. The weak sulphur-liquor is pumped up into a just oxidized, dry tank, and in this becomes strong, so that it runs off at the bottom as strong liquor. The lixiviation is then continued with fresh water, and the resulting liquid collected as weak sulphur-liquor, as soon as its specific gravity falls below 13° Tw.; when it falls below 1½° Tw. the feed of water is stopped.

This process is evidently much more troublesome than the usual soda-lixiviation; and partly for this reason, but especially for the sake of greater cleanliness, it is now preferred to carry on the sulphur-recovery in separate sets of tanks, which causes a little more expenditure for labour, but makes the process comparatively independent of the soda-lixiviation.

At least three alternate oxidations and lixiviations will be necessary; six will be advantageous, in order to recover as much sulphur as possible. The oxidizing lasts from 14 to 16 hours, the lixiviation 10 to 12 hours; from this the size and number of the tanks can be computed for each works. For three oxidations the

sulphur-recovery process really takes twice as many tanks as the soda-lixiviation, and for further oxidations more in proportion. [Mond allows 72 hours for three oxidations and lixiviations, which means only half as much tank-space again as for the soda-lixiviation, the latter usually taking 48 hours; but that hurries the process too much, and frequently causes embarrassment.]

It is very important that the sulphur-liquors shall always possess the *proper composition*; and this is more usually attained by regulating the strength of the current of air, its duration being left unchanged. Mond has paid special attention to this matter, and has indicated simple analytical methods for testing the sulphur-liquors. The liquors are theoretically right when on adding a strong acid exactly 2 H_2S and 1 SO_2 are liberated from them, which at the moment of liberation decompose to $2H_2O+3S$, and thus yield water and sulphur but no gas. First it is ascertained how much decinormal iodine solution a certain volume of the sulphur-liquor requires to turn a starch solution blue, and then how much iodine is required for the same volume after zinc acetate has been added and the precipitate of ZnS has been filtered and washed. It is better to take the double volume, add the zinc solution, dilute to 100 c. c., filter through a dry filter, and employ 50 c. c. for titrating with iodine. In the former case the polysulphides, sulphhydrate, and hyposulphite are estimated together, in the second only the last. The reactions are:—

1. $CaS_x+2I = CaI_2+S_x$;
2. $Ca(SH)_2+4I = CaI_2+2HI+2S$;
3. $2CaS_2O_3+2I = CaI_2+CaS_4O_6$.

If we compare these equations with those representing the decomposition by acids, we find:—

a 1. $CaS_x+2HCl = CaCl_2+H_2S+S_{x-1}$;
a 2. $Ca(SH)_2+2HCl = CaCl_2+2H_2S$;
a 3. $2CaS_2O_3+4HCl = 2CaCl_2+2SO_2+2S+2H_2O$.

Consequently, according to both 1 and 2, each H_2S corresponds to two I; but in 3 to SO_2 only one I. Since we know that there ought to be 2 H_2S to 1 SO_2, it follows that, for four atoms of iodine required for polysulphides and sulphhydrates, only one of iodine

ought to be taken up by hyposulphite. Hence the iodine required for the original sulphur-liquor ought to be *five times* as much as that required for the liquor after precipitation by the zinc salt. This proportion will, of course, be accurately attained only exceptionally; it should be approached as nearly as possible: but, in order to avoid the escape of H_2S in the further treatment, any excess ought to be on the side of the hyposulphite; and hence the second figure ought to be rather more than one fifth of the first.

It is also possible to calculate the total sulphur contained in the liquor and the quantity of HCl required for precipitating it. To a certain quantity of the liquor, say 3·2 c. c. ($= \frac{1}{10}$ equivalent of sulphur in c. c.), a little starch solution is added, and then decinormal iodine till it turns blue. The liquid is decolorized by a drop of sodium-hyposulphite solution, a little litmus added, which will turn it red, and decinormal soda solution run in till it turns blue. According to the above equation No. 2, the hydriodic acid set free (and accordingly the standard soda used in the last titration) corresponds to the quantity of sulphhydrate. The hyposulphite is found by a separate titration with iodine after precipitation by zinc salt; and when both are deducted the polysulphide is left. If we employ for each iodine titration 3·2 c. c. sulphur-liquor, and assume with Mond that the polysulphide is chiefly CaS_2 (this is not correct, as we shall see below, but quite sufficiently near the truth for practical purposes), we reckon as follows. We add up the cubic centims. of iodine solution required for both titrations, deduct the cubic centims. of decinormal soda solution, and divide by 10; this shows the percentage of sulphur in the liquor. It arises in this way:—CaS_2 furnishes for each cubic centim. of decinormal iodine 0·0032 S; $Ca(SH)_2$ only half as much, for which reason we deduct the decinormal soda required for neutralizing the corresponding quantity of HI formed; CaS_2O_3 furnishes twice as much, for which reason the iodine used up in titrating for hyposulphite alone is added to that used up for the original liquor. The usual percentage of the liquors is 4 to 7 per cent. sulphur.

Another plan, elaborated by Wahlert (Dingl. Journ. cxcii. 63), permits estimating the sulphur of the polysulphide, but requires for its execution as many hours as that of Mond takes minutes. He decomposes the liquor by passing through it a current of CO_2 till the decomposition of the sulphides is complete, estimates the sulphur in the precipitate by weight after dissolving the $CaCO_3$, and in the

filtrate the hyposulphite by iodine solution. In a separate sample he estimates by ammoniacal silver solution the quantity of sulphur driven off as H_2S by acids. The exact method of Stahlschmidt, which is far too tedious for factory use, will be mentioned below.

From the quantity of sulphur that of muriatic acid can be easily calculated, since each 32 S requires 36·5 HCl. But, according to Mond, less acid than that calculated is always used, certainly not to the advantage of the process, since by the formation of trithionic and a little pentathionic acid a portion of the sulphur is always lost as calcium sulphate. Mond represents the decomposition of calcium hyposulphite as different from that stated in all chemical treatises and assumed in Schaffner's process (viz.—

$$CaS_2O_3 + 2HCl = CaCl_2 + SO_2 + S + H_2O);$$

he asserts that comparatively little sulphur and next to no sulphurous acid are formed, but chiefly trithionic and a little pentathionic(?) acid, by the reaction

$$5CaS_2O_3 + 6HCl = 3CaCl_2 + 3H_2O + 2CaS_3O_6 + 4S.$$

On boiling, the trithionate is decomposed into calcium sulphate, sulphur, and sulphurous acid. The latter converts the undecomposed portion of the hyposulphite into trithionate, by the well-known reaction

$$2CaS_2O_3 + 3SO_2 = 2CaS_3O_6 + S.$$

The newly formed trithionate again decomposes, and so forth. Owing to these reactions, a solution of calcium hyposulphite can be completely decomposed into S, $CaSO_4$, and very little SO_2, if it be heated to boiling and a quantity of acid be added to it sufficient for saturating half of the calcium dissolved. Where muriatic acid is very valuable, Mond proposes to act in this way; but otherwise he does not advise it, because much sulphur is lost as gypsum, and this makes the recovered sulphur very impure.

This matter has been more closely investigated by Stahlschmidt (Dingl. Journ. ccv. p. 229). He draws attention to the almost forgotten former experiments of Schöne (Poggend. Annal. cxvii. p. 58), which prove that calcium cannot exist in solution with less than 4 molecules of sulphur; if less than 3 mol. of sulphur to 1 mol. of CaS are brought into contact with water, only so much

CaS is dissolved that CaS_4 can be formed, the remaining CaS being indifferent and forming with water $Ca(OH)_2$ and $Ca(SH)_2$. The former is partially, the latter entirely dissolved along with the CaS_4. The latter can dissolve another molecule of sulphur, with heat even more; and it is very apt to crystallize together with more lime. Herschel obtained such a compound having the formula

$$3CaO, CaS_4 + 12H_2O;$$

according to Schöne this can only be formed in the presence of an excess of lime and calcium hyposulphite. The crystals made by H. Rose were also obtained by Schöne; he does not, however, like Rose, assume the presence of CaS_5 in them, but gives them the formula

$$4CaO, CaS_4 + 18H_2O \text{ (calcium oxytetrasulphide)};$$

they are always formed whenever CaS_4 meets with $Ca(OH)_2$ and $Ca(SH)_2$. Most probably this salt is always present in the sulphur-liquors, where all the conditions for its formation exist, along with CaS_5; lower sulphides are excluded; but in some conditions Herschel's salt might occur in them as well.

Besides calcium compounds, there must always be sodium compounds in sulphur-liquors, which should not be overlooked when analyzing these; tank-waste mostly contains a considerable percentage of soda [most of it certainly in an insoluble form; but a portion of it doubtless will become soluble during the oxidation].

Stahlschmidt found Rose's salt (as the author has also done) in a sulphur-liquor kept for several months with exclusion of air, in splendid orange-red needles 3 to 5 inches long; on analysis he found Schöne's formula confirmed. The same compound can be precipitated momentarily from sulphur-liquor by alcohol in the form of coruscating scales and needles, and that in large quantity. If the air is not completely excluded, the crystals decompose in the liquor. Moreover Stahlschmidt obtained from the liquors, deprived of the oxytetrasulphide by alcohol, by further addition of alcohol, a white precipitate of calcium sulphite ($CaSO_3 + \frac{1}{2}H_2O$), and, in the last portion of the precipitate, also calcium hyposulphite. The calcium sulphite once precipitated did not dissolve again in fresh liquor; hence Stahlschmidt supposes it to exist as the compound $CaSO_3 + 2CaS + 6\,aq$, which Kuhlmann had accidentally noticed, in the shape of yellow crystals, on old tank-

heaps (see p. 633), and which is split up by alcohol. In the last mother liquors, after several months a crystallization of sodium hyposulphite set in; but the presence of either trithionic, or tetrathionic, or pentathionic acid could not be proved. The occurrence of free sulphur, dissolved by the calcium polysulphides, was proved by shaking with carbon disulphide, that of calcium and sodium sulphhydrates by the evolution of H_2S with a solution of manganese. Besides, CaS_5 and CaS_4 can be detected by analysis. Hence there are found in the liquors:—CaS_5; $4CaO$; $CaS_4 + 18\,aq$; $CaSO_4$; $CaSO_3$; $Na_2S_2O_3$; $NaHS$; $Ca(SH)_2$; and S.

Stahlschmidt's analytical method was as follows.

For estimating the hyposulphite and sulphite he does not, as usual, precipitate the sulphides by a zinc salt, but by neutral $MnCl_2$, because MnS is more easily washed; or else, like Wahlert, he precipitates with CO_2 and boils: in both cases the filtrate is titrated with iodine solution, which indicates SO_2 together with $S_2O_3H_2$, since the H_2S must at once transform the former into the latter. Another portion of the liquor is precipitated with absolute alcohol, the precipitate first washed with alcohol, then with water, in order to redissolve the calcium and sodium hyposulphite also precipitated; and the $CaSO_3$ remaining on the filter is titrated directly by iodine; its quantity is subtracted from that previously found by iodine; but only half of the quantity of iodine found in the second case must be calculated, because hyposulphite only requires half as much iodine as sulphite. Thus the hyposulphite originally present is ascertained. [What becomes of the calcium oxytetrasulphide also precipitated by alcohol?] In separate portions of the liquor the sulphuric acid is estimated by barium chloride, the total lime by ammonia and ammonium oxalate, the total soda as NaCl by boiling with hydrochloric acid, filtering off the sulphur, and precipitating the lime as oxalate; the total sulphur by adding solid $CuCl_2$, in order to fix the H_2S, and oxidizing with fuming nitric acid; the sulphhydrate by Mond's process indicated above. The polysulphides are calculated from the difference, by deducting from the total sulphur the sulphur of the sulphites, hyposulphites, and sulphates; also from the total lime the calcium of the sulphite, sulphate, and sulphhydrate. [The hyposulphite is assumed by Stahlschmidt to exist exclusively as a sodium salt, because, after treating with CO_2 and boiling, no reaction for lime could be obtained in the liquid.] The two numbers thus obtained

for calcium and sulphur yield 1 molecule of Ca to 1·9 molecule of S; but it cannot be assumed that CaS_2 occurs in the liquors, for the reasons above quoted; and it must be assumed that $4CaO, CaSO_4$ is present, along with about 1 molecule of CaS_5, as the calculation shows. [It must be acknowledged that the assumption of Mond, that the liquors contain CaS_2, is practically sufficient for calculating the sulphur contained in them.] Altogether the liquor examined by Stahlschmidt contained in 25 cub. centims.:—

CaS_5	0·309	gram.
$4CaO, CaSO_4 + 18$ aq.	1·106	„
$CaSO_4$	0·0333	„
$CaSO_3$	0·275	„
$Na_2S_2O_3$	0·8453	„
CaH_2S_2	0·0704	„
NaHS	0·3869	„
S	0·1213	„

[This analysis should be compared with that made in the author's laboratory, p. 660, which was performed by a process somewhat different from Stahlschmidt's, and described in Dingl. Journ. ccxxviii. p. 258.]

With reference to the decomposition of the sulphur-liquor by hydrochloric acid, Stahlschmidt adopts the opinion of Mond, according to which the large quantity of calcium sulphite found in the precipitated sulphur is to be ascribed not merely to the sulphuric acid present in the muriatic acid, but to the formation and subsequent decomposition of trithionic acid. Pure SO_2 acts upon sulphur-liquor so that the sulphides are completely decomposed with separation of S and H_2S, with which it at once forms hyposulphites. This plan, long ago opened out by Schaffner, is excellent for manufacturing sodium hyposulphites. If more SO_2 is passed into the liquor, when already neutralized by SO_2 and filtered, no separation of sulphur takes place; hence the calcium hyposulphite is not decomposed any further. But on heating, very soon calcium sulphate and sulphur are precipitated. *Pure* calcium hyposulphite is not decomposed in this way on heating its solution, but chiefly according to the equation

$$CaS_2O_3 + H_2O = CaSO_4 + H_2S;$$

it is otherwise when SO_2 is present, because then the conditions

are given for forming calcium trithionate, which is first formed and on heating is decomposed into $CaSO_4$, SO_2, and S. The same occurs when calcium or sodium hyposulphite is mixed with but little HCl; for then the SO_2 liberated acts upon the unchanged salt as above; but when all the HCl necessary for decomposing the salt is added *at once*, no formation of $CaSO_4$ takes place. "Sulphur-liquor" behaves quite similarly, except that by gradual addition of HCl first the sulphide and sulphhydrate are decomposed with evolution of H_2S, and only at the end is SO_2 formed as well. The proportion between liquor and acid ought to be such that no SO_2 is in excess; thus the smallest quantity of gypsum is formed. If, however, after the transformation of all the sulphide and sulphhydrate into hyposulphite SO_2 is still present, trithionate is formed, and by its decomposition sulphur is lost as gypsum. In Schaffner's process the formation of trithionate and consequently of gypsum on decomposing the liquor, treated with SO_2, by HCl seems to result from the oxidized waste being especially rich in hyposulphite, which liberates much SO_2 on the decomposition of the liquor by HCl.

The author cannot consider Stahlschmidt's last opinion conclusive. To the formation of trithionic acid (on which he lays and Mond formerly laid so much stress) the hyposulphite originally present in the liquor must be indifferent, since in Schaffner's process *all* the sulphur compounds (except the sulphates) are converted into hyposulphites before the hydrochloric acid acts upon them. An original excess of hyposulphites in the liquor could act injuriously only in this way—if during the action of SO_2 upon the liquor, converting its sulphide and sulphhydrate, a considerable quantity of SO_2 remained dissolved without alteration, and then gave rise to the formation of trithionic acid. But this might be easily remedied by partly or entirely omitting to expel the SO_2 from the liquor treated with HCl, which cannot do much harm; moreover Schaffner himself points out that the composition of the liquor to be aimed at is that in which, for $1SO_2$, $2H_2S$ are given off, just as Mond wishes, in which case no excess of SO_2 is present. Moreover Schaffner employs heat only at the end of the operation, in order to expel the SO_2. Trithionic acid has never been proved to be present as such; and its formation is spoken against by experiments (unpublished) of Schaffner's with pure hydrochloric acid, as well as by the author's own (p. 664), in which *no* $CaSO_4$ was formed.

If indeed it should be confirmed that in Schaffner's two-boiler apparatus more gypsum is formed than in Mond's process, of which the absolutely contrary is asserted by Schaffner from his own experience, in the author's opinion this could only be caused by the fact that in Mond's agitating-tub the sulphur-liquor receives the necessary HCl all at once, in Schaffner's apparatus only gradually. That the temperature of 60° C., necessary in Mond's process, is not required by Schaffner when passing in the SO_2, speaks for the latter and against the former, so far as trithionic acid is concerned. Direct experiments upon this matter are not before the public; and thus not even the fact, let alone its cause, can be established, whether in one of the processes more gypsum is formed than in its rival. The author's own experiments did not indicate any formation of trithionic acid even on gradual addition of HCl and at a raised temperature; it could only be established when free SO_2 was in contact with hyposulphite *for some time*, or when (which comes to the same) an insufficient quantity of HCl was employed for decomposing sulphur-liquor.

Mond's ordinary decomposing-process (which is the only one employed in practice) is as follows. A little sulphur-liquor, which, as mentioned above, should contain two molecules of sulphide to one of hyposulphite, is added to a little acid till there is a slight excess of sulphide; then sufficient acid is added to saturate the total calcium; a quantity of liquor equivalent to the last acid is added; then again acid, then liquor, and so forth till the vessel is filled. At last only half of the acid needed is added, and steam is blown in till the temperature has risen to 60° C. Above this more gypsum is formed; below 40° C. H_2S escapes, and the sulphur does not settle well. All this is much simpler in practice than it appears on paper.

The operation is carried on in a wooden tub provided with a mechanical agitator and an open steam-pipe. This tub is first a quarter or one third filled; best of all, sufficient $CaCl_2$ solution from the last operation is left in. By blowing steam in, the temperature is raised to 60° C. Now a stream of muriatic acid and another of sulphur-liquor are run in at the same time below the surface of the liquid, regulated so that a very slight excess of acid remains in the liquid. This is recognized by pouring a few drops of sulphur-liquor into a sample of the milky cream-coloured liquid, which ought not to change its colour; but a few drops more (the free acid now being

saturated) should turn the colour grey, by precipitating a little FeS from the $FeCl_2$ always present. (Mond formerly prescribed a small excess of sulphur-liquor.) The muriatic acid may be dilute, down to 5° or 6° Tw., *e. g.* the weak acid from post condensers mixed with a little strong acid. The applicability of weak acid is a great advantage of Mond's continuous precipitation-process. The colour of the liquid where the sulphur-liquor enters will necessarily be that of the latter (that is, yellow or dark green); from that place towards the inlet of the acid it becomes black, grey, milk-white, at last (close to the acid-pipe) as yellow as butter. If the proportion between acid and liquor is right, the colours will constantly keep their places, and, for instance, the grey colour not come nearer to the acid-pipe or go further away from it.

The tub must be covered over; the agitating-shaft passes through the centre of the cover, which also has a manhole and a gas-pipe. The latter is connected with a chimney in order to take away any gas; but in a properly conducted operation no gas at all ought to escape. At the commencement of the operation some H_2S may easily escape; but this can be prevented almost entirely by beginning with a certain bulk of liquid, especially if it contains rather more hyposulphite, and at once raising its temperature to 60° C., which temperature must be maintained all through, but never exceeded by more than about 5°.

When the tub has been run quite full, the agitator being kept constantly going, about two thirds of its contents are run out through a plug-hole in the bottom. This liquid, a solution of $CaCl_2$ with a little free acid, holding sulphur and gypsum in suspension, is run upon the filter by means of a shoot. Another way of working is:—Fixing an earthenware pipe in the side of the tub a foot above the bottom, ending in a cock or an india-rubber tube and clamp, through this, as soon as the tub is full, as much of the muddy liquid is continuously run off as is supplied at the top; but then both the liquor- and the acid-pipe must end just below the surface of the liquid, so that the decomposition may be perfect before the mixture gets to the running-off pipe. This must be checked by pet-cocks put in at different heights from the bottom. The most suitable plan seems to be that introduced by Kraushaar at Thann (Dingl. Journ. ccxxvi. p. 415). A wooden tub, 6 feet 6 inches in diameter and 5 feet high, is provided with an agitator made of iron and wood; the liquor enters from an iron

pipe outside the tub, close above its bottom, and the acid through a wooden pipe inside, so that liquor and acid meet at the same point near the bottom of the tub. The heating is done by a steam-pipe entering from the outside. A beginning is made by half-filling the tub with water, heating this to 70° C., and starting the agitator. Now sulphur-liquor and acid are run in in such proportions that the liquid remains acid, but a sample of the same, after settling, gives only a very slight precipitate on adding more acid [*sic*; no doubt it should be "more sulphur-liquor"]. This proves that no free HCl is present as yet, but only SO_2. The tub has a lateral overflow-pipe 12 inches below its top, through which the solution of $CaCl_2$ and the S run away when they have risen to that level. The tub accordingly always remains filled up to that height, even at night when the work is stopped; and H_2S can never escape (as several years' work has shown), since on rising in the liquid it has an opportunity of decomposition with the SO_2 always present in excess. The liquid running away mostly smells of SO_2, because on oxidizing the waste a small excess of hyposulphite is preferred to an excess of the more troublesome H_2S.

The separation of the sulphur from the mother liquor, containing chiefly $CaCl_2$, along with small quantities of CaS_2O_3, free SO_2, &c., can either be effected by running the muddy liquid upon a wood filter, the lath bottom of which is covered with sail-cloth, or it is run through a series of settling-vessels, entering on one side at the top, and leaving again at the top on the other side. On passing across, the largest portion of the sulphur deposits already in the first settler; three will mostly suffice for obtaining a perfectly clear liquid at the end. This process does not permit washing the sulphur at the same time (which is not necessary with Schaffner's melting process), but is less troublesome than the easily stopped-up sail-cloth filters, which mostly allow some of the finely divided sulphur to pass through and thus after all necessitate separate settlers.

Mond expresses the final result of the reactions which take place in his mixing-tub by the following formula (translated into modern notation):—

$$CaS_2O_3 + 2CaS_x + 6HCl = 3CaCl_2 + 3H_2O + (2+x)S.$$

[It should be $(2+2x)S$.]

But, according to him, the actual reaction is very different from

that formula, since probably all the sulphur acids are formed, especially in consequence of the action of the hyposulphurous acid and the sulphurous acid formed by it. All these polythionic acids are reconverted into hyposulphite by the calcium sulphide of the sulphur-liquors added:

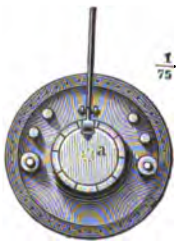
$$3S_xO_2 + 2CaS_y = 2CaS_2O_3 + (3x + 2y - 4)S;$$

$$3S_xO_5 + 5CaS_y = 5CaS_2O_3 + (3x + 5y - 10)S.$$

When more HCl is added, only hyposulphurous acid and its products of decomposition are formed, which are again converted, without any evolution of gas, into sulphur and hyposulphite, of which in the end a slight excess remains. This by an insufficient addition of HCl is converted into sulphate and sulphur. In practice about 90 per cent. of the calculated quantity of acid is required for completely decomposing a liquor of proper composition; but if an excess of hyposulphite is present, less acid is used [in other words, more sulphur is lost as gypsum]. Thus 90 per cent. of the sulphur contained in the liquor is obtained in a nearly pure state; after filtering and washing out the $CaCl_2$ it need only be melted up in an iron pot to obtain an article with no more than 0·1 to 1 per cent. impurities. If in the place of ordinary muriatic acid the acid still-liquors from the old manufacture of chlorine are employed, a dark-coloured sulphur with 5 per cent. impurities is obtained. [On the large scale the latter was never done, even before the recovery of manganese had become general.]

The above description by Mond (1867) refers to his first prescription, according to which a slight excess of sulphur-liquor was to be employed, while afterwards he found it more suitable to proceed as described by us previously, viz. leaving a small excess of acid. Whichever way the work be done, there is always far too much gypsum in the precipitated sulphur for the latter to be purified by simple fusion; consequently all the factories working by Mond's process have adopted Schaffner's melting under water by steam-pressure. Many apparatus are employed for this; none of which come up to Schaffner's in facility of manipulation. We shall accordingly only give a sketch of the apparatus employed by several English works. Fig. 261 represents the cover, seen from the top; fig. 262 is half a front elevation, half a section. The melting-vessel is of cast iron, open at the top, with semiglobular

Fig. 261.



$\frac{1}{75}$

Fig. 262.

$\frac{1}{75}$

bottom, 4 feet 6 inches wide and 8 feet high. The cover, strengthened by ribs and fastened by many screw-bolts, has a diameter of 5 feet 4 inches. In its centre there is a man-hole with a lid, *a*, 2 feet 4 inches wide, fastened by swivel-bolts. A steam-pipe *b* ends at the bottom of the vessel in a perforated ring; another pipe *c*, open at the bottom and provided with a cock immediately above the cover, serves for blowing off the melted sulphur at the end of the operation by means of the steam pressure existing in the apparatus. As soon as the steam changes into a muddy watery liquid, its direction is changed. Here certainly Schaffner's agitator, and with it some trouble in renewing bearings &c., is saved; the steam-jacket can also be easily replaced by a separate envelope. But, on the other hand, it easily happens, when the steam-pressure in the main pipe sinks, that the liquid sulphur is driven back into the main steam-pipe by the higher pressure within the apparatus. To prevent any great damage from this, there ought to be a back-pressure valve, opening towards the melting-pot, but automatically closed by the sulphur when forced back.

Mond in 1867 stated the yield of sulphur by his process at 10 to 11 per cent. of the sulphate employed in the black-ash mixture —*i. e.* half of the sulphur contained in the same, or 60 per cent. (in 1868 he says only 50 per cent.) of the sulphur contained in the tank-waste. [The difference of 10 per cent. is owing to the sodium sulphate going away in the soda-ash.] This amount is a maximum, only attained by many oxidations and lixiviations. At Stolberg

16 per cent. on the soda ash is obtained, which about equals the above figure; but usually less than that is recovered. The cost of the process is stated by Mond at £1 per ton of sulphur; but this is only for labour and fuel, and nothing is calculated for muriatic acid, of which *at least* 3 parts of the strongest kind are required for each ton of sulphur. Even without calculating the acid, Mactear states the cost price of the sulphur recovered by Mond's process at Tennant's works at three times the sum mentioned by Mond himself.

As is easily seen, the stages of Mond's and Schaffner's process are interchangeable without any detriment to the principle of sulphur-recovery; and in many respects this has actually been done. Thus Schaffner has taken from Mond the carrying-on of the subsequent oxidation in the tanks themselves, whilst retaining, for good reasons, the first oxidation in heaps. On the contrary, the factories working by Mond's process have so much felt the disadvantage of employing the same set of tanks for lixiviating black ash and recovering sulphur, that they frequently, like Schaffner, carry on these operations in separate sets of tanks. Muddy waste, at any rate, cannot be oxidized in the tanks, but only in heaps. The second stage, that of precipitating by muriatic acid, is mostly effected by Mond's plan, recently even at Schaffner's works, although for smaller works Schaffner prefers his own plan. For the last stage, that of purification, Schaffner's melting under water has been adopted everywhere. Hence the sulphur-recovery process as carried on in most places must be regarded as a combination of several features taken from both processes.

P. W. Hofmann's Process.

The only other method of sulphur-recovery which has been carried out in practice for any length of time is that of P. W. Hofmann, worked out at Dieuze with the assistance of E. Kopp and Buquet, and patented in 1866. A tank-heap of thirty years' accumulation draining into a watercourse, the owners were compelled to seek for a process by which the tank-waste might be rendered harmless. Without detaining ourselves with the initial stages of this process, we will describe it after the accounts most recently given by E. Kopp (Wurtz, Dictionn. de Chimie, ii. p. 1593), Tiemann (Hofmann's Bericht, i. p. 484), Buquet (Dingler's Jour-

nal, cxci. p. 304), Rosenstiehl (*ib.* p. 464), Richters (*op. cit.* cxcii. pp. 64, 133).

Hofmann's process, as we shall see, is founded upon the employment of the acid manganese still-liquors. Since at the time of his invention these were as bad a nuisance as the tank-waste, there was some justice in considering this a special merit, as Kopp does; but the same thing could not but lead to great complications by making one part of the process dependent on the other: to works where no chlorine was made, it was inapplicable from the first. Since at the present time the chlorine still-liquors are no longer a waste product injurious to health, but serve for the recovery of manganese peroxide, this fact alone would prevent the extension of Hofmann's process.

The principles of this process are these:—The tank-waste is oxidized in heaps, but the oxidation hastened by introducing a certain quantity of iron and manganese sulphide. This is done by pumping chlorine still-liquors, neutralized in a way described below, into a tank, one corner of which is fenced off by wickerwork in order to retain any rough solid bodies. The tank is three-quarters filled up; and, with constant stirring, 5 or 6 tons of tank-waste are thrown in, till all the iron has been thrown down as FeS; this is shown by a sample of the filtered liquid with sulphur-liquor yielding, instead of a black or grey, a flesh-coloured precipitate of MnS. A large excess of waste is employed, which mechanically carries down the FeS, without precipitating much manganese. The waste remains impregnated with manganese-liquor, which very much quickens its oxidation, as well as that of more waste with which it is mixed,—the oxidation then occupying only six or seven days, instead of three weeks, as in Schaffner's case. The way in which FeS and MnS assist the oxidation we have seen, p. 455.

The heaps, 50 feet long, from 10 to 13 feet broad, and 5 to 6 feet high, are turned over several times, and gradually brought nearer to the lixiviating-tanks, which are made in brickwork in cement with wooden false bottoms, three combined to form a set. Each tank holds a day's work, along with 30 tons of water. By washing the waste first with weak sulphur-liquor, then with water for three days, a liquor of 23° Tw. is obtained, very rich in polysulphides. These "first yellow liquors" contain in 100 parts 6·516 S, 2·468 Ca, 0·172 Cl. The residue is thrown out, oxidized

for three days in the air, and again lixiviated, yielding the "oxidized yellow liquors" of 21° to 25° Tw., rich in hyposulphite, and employed for neutralizing the acid still-liquor, along with a little of the first liquor. Analyses by Wöhlert (Dingl. Journ. cxcii. p. 64) do not, however, show a very great difference between the two liquors. The new residue is cast upon a heap; it still becomes strongly heated on lying, but is said to yield no more coloured drainage. Kopp mentions only two, Tiemann three oxidations.

The chlorine still-liquors, which now come into play, contain chiefly free chlorine, HCl, Fe_2Cl_6, and $MnCl_2$. They are "neutralized" by mixing them with such a proportion of yellow liquor that some excess of SO_2 remains. Since the mixing cannot be done so accurately as to avoid all evolution of H_2S, it is performed in an air-tight lead apparatus, the H_2S gas is conducted through a wood fire, burnt to SO_2, and this is absorbed by "first yellow liquors." A good deal of sulphur is precipitated by the free Cl and HCl, and by the reduction of Fe_2Cl_6 to $FeCl_2$; it is coloured grey by some FeS; and 56·8 kilog. per cubic metre of yellow liquor (about 5 per cent. by weight) are obtained. It is filtered, washed, and dried. The "neutralized" still-liquor is now cleared of iron in the manner mentioned in the beginning of this description, after which it contains only $MnCl_2$ and $CaCl_2$. It is completely settled, and "first yellow liquor" run in; flesh-coloured MnS, mixed with the excess sulphur of the polysulphides, falls down. Any hyposulphite contained in the liquor is lost, since it does not precipitate the manganese. [This loss and that of the H_2S of the sulphhydrates, which also causes a great nuisance, are serious drawbacks to the process.] The precipitate obtained contains about 55 MnS, 40 free sulphur, and 5 Mn_2O_3 (58·6 per cent. S), which approaches the proportion of 1 Mn to 3 S.

The ultimate residue, after being exposed to air for some time, is said by Hofmann to contain no CaS, but 66 per cent. $CaSO_4$, 31 $Ca(OH)_2$ with a little $CaCO_3$, Al_2O_3, Fe_2O_3, Mn_3O_4, &c. But no other chemist has found such residues free from oxidizable sulphur compounds, even when weathered for some years. Richters (whose analyses are detailed in 'Dingler's Journal,' *l. c.*) found 22 to 29 per cent. calcium sulphite, and up to 6 per cent. hyposulphite, in them.

The MnS quickly turns brown in the air, and oxidizes in an analogous manner to FeS, viz. forming Mn_2O_3 and free sulphur.

Richters (*l. c.*) gives detailed analyses of the oxidized product—which, by the way, prove that it still contains about ½ per cent. of Fe_2O_3. It is easily burnt in the ordinary brimstone-burners. The residue weighs about one half of the quantity employed, and, according to Hofmann, contains 44·5 $MnSO_4$, 18·9 MnO_2, 36·6 MnO: more exact analyses are given by Richters. Thus a good deal of sulphur still remains in this residue; say, 20 to 25 per cent. of the total sulphur. According to Rosenstiehl's proposal it is mixed with an equivalent of nitrate of soda, and heated in the same burners as before; the nitrous gas given off is conveyed into vitriol-chambers; and the residue now consists of sodium sulphate and an oxide of manganese corresponding to 55 per cent. MnO_2. By first exhausting with water the residue from burning the MnS, boiling down the solution, drying, and heating with $NaNO_3$, a product equal to 70 per cent. MnO_2 can be obtained. The sodium sulphate contained in the washings from the manganese is boiled down to dryness or worked up for "pearl hardening" (p. 576). The manganese oxide is said to be very well adapted for glass-works, because it is free from iron; but the demand for such is very little; nor can it be said to be quite free from iron, as Richters has shown.

Buquet (*l. c.*) states the following yields from a factory turning out daily 20,000 litres of still-liquors and 30 tons of tank-waste, viz. 1·4 ton of pure (?) sulphur, 2·2 tons of sulphur in metallic sulphides, 0·77 ton of manganese oxides containing 60 per cent. MnO_2, 20 kilog. of calcium hyposulphite, and 0·6 ton of calcium sulphate. The cost price of sulphur is said to be 40 to 50 francs per ton. These statements, proceeding from an "inventor," must be received with the usual caution.

P. W. Hofmann's process is evidently extremely complicated; and this would appear even more clearly from a more detailed description than we have given. It is, moreover, dependent upon using up still-liquors, which nowadays are nowhere a waste product, and upon utilizing the MnS and nitrous gas for vitriol-making. There is always a loss of nitre in that operation; nor can the vitriol-chambers do with only as much nitrous gas as the recovery of manganese would supply; consequently nitric acid would have to be made by admitting air and water. This plan has failed entirely, and has been given up even at Dieuze. In any case a large portion of the manganese was lost along with the oxidized tank-waste; and that which was recovered was only a very inferior article

for chlorine-making. The solution of sulphate of soda would rarely pay for boiling down. The yield of sulphur must, from the causes above mentioned, have been much less than in Mond's or Schaffner's process; it was very impure; and the cost of labour must necessarily also have been much greater than in either of these two processes. These drawbacks have led to the abandonment of the process everywhere except at Dieuze, where it is said to be partially employed yet.

Complete Recovery of Sulphur and Lime from Tank-waste.

We shall conclude this Chapter by describing *in extenso* the new process of Schaffner and Helbig (patented in England, March 9th, 1878), which, if it succeeds as well in the long run as it has done hitherto, seems destined to put the final touch to Leblanc's process, since it entirely does away with the only serious drawback attached to that process, viz. the tank-waste.

The sulphur-recovery processes hitherto in use are based essentially on oxidizing the tank-waste to a certain extent, dissolving out the sulphur-liquor, and precipitating the sulphur by muriatic acid. In the best case, however, only 50 to 60 per cent. of the sulphur are thus recovered; the other 40 to 50 per cent., together with lime, form a new waste, containing undecomposed calcium sulphide along with sulphite and sulphate. This new waste is not a nuisance similar to fresh tank-waste; but, owing to its great bulk and its very slight utility, it is a great burden upon alkali-works. This will be done away with by the invention of Schaffner and Helbig, which recovers by far the greatest portion of the sulphur and also the lime.

It is chiefly based on (*a*) the applicability of magnesium chloride, hitherto not employed in the arts, to decomposing calcium sulphide—thus,

$$\text{I. } CaS + MgCl_2 + H_2O = CaCl_2 + MgO + H_2S$$

(calcium carbonate not being acted upon by $MgCl_2$); (*b*) the recovery of the magnesium chloride by exposing the residue from the first operation (consisting of magnesia, calcium chloride, and the impurities of soda-waste), after driving off the H_2S, to the action of

carbonic acid, by which calcium carbonate and magnesium chloride are formed—thus,

$$\text{II. } MgO + CaCl_2 + CO_2 = MgCl_2 + CaCO_3.$$

A portion of the magnesium chloride can be replaced by the simultaneous action of muriatic acid, by which the separated magnesia is always dissolved again, and again becomes active. This reaction might be applied where an excess of muriatic acid is obtained, and at the same time yields calcium chloride in case the latter is not got otherwise as a by-product. In this case the mud, after being treated with boiling water, is allowed to settle, and a corresponding portion of the clear $CaCl_2$ liquor is drawn off. Of course the action of CO_2 can only recover as much $CaCO_3$ as corresponds to the $MgCl_2$ employed.

(*c*) The sulphuretted hydrogen escaping in the first operation is transformed into sulphur by means of sulphurous acid :

$$\text{III. } 2H_2S + SO_2 = 3S + 2H_2O.$$

Ordinarily this reaction does not take place as smoothly as the formula would indicate, but, as we have seen before, large quantities of pentathionic (or tetrathionic) acid are formed; and it would fail to be available in this case, as it has done in all previous cases, unless Schaffner and Helbig had discovered a plan for preventing to a great extent the formation of pentathionic acid, or, if the latter has been formed, precipitating the sulphur from it*. This consists in the application of solutions of calcium or magnesium chloride, also of other mineral salts and acids (comp. p. 647). If aqueous solutions of H_2S and SO_2 are mixed in the proportions expressed by the above equation, a milky liquid is formed, from which by addition of a solution of calcium or magnesium chloride, a flaky, readily settling precipitate is obtained, which corresponds to the theoretical quantity. An excess of one gas or the other is found unchanged in the liquid, and does not interfere with the reaction. It is not yet known what part the chlorides play in this case; but so much is certain, that an amount of $CaCl_2$ or $MgCl_2$ equivalent to the total sulphur is required.

The greatest impediment to the application of the mutual decomposition of H_2S and SO_2, which, even more than the formation of polythionic acids, had baffled all previous endeavours in this direc-

* Comp. p. 645 as to the confusion of pentathionic with tetrathionic acid.

tion, was the milky state in which the sulphur is precipitated, which prevents its separation by subsidence or filtration. This is completely obviated by the employment of solutions of salts (as stated above), which is the most important feature of the new process.

The $MgCl_2$ obtained in the second operation is employed for decomposing new quantities of tank-waste, and the calcium carbonate in the black-ash mixture.

The operations are practically carried out as follows. The decomposition of tank-waste by magnesium chloride takes place in a large, air-tight, iron vessel provided with an agitator, with contrivances for charging and discharging the materials, gas-delivery pipes, &c. Here the mixture is exposed to heat. Either the tank-waste is gradually introduced into a charge of $MgCl_2$, or, inversely, the $MgCl_2$ solution is run upon the waste, or both are simultaneously introduced in equivalent proportions. The apparatus must be so arranged that the operation can be arrested at a moment's notice; nor should any H_2S be able to escape into the air: this is prevented by producing a draught from without by means of a chimney, fan-blast, or pump, and by always keeping an excess of SO_2 in the decomposers over and above that corresponding to the arriving H_2S, so that the latter can never be in excess. According to Stingl and Morawski this process is to be explained thus: first magnesium chloride and calcium sulphide decompose into calcium chloride and magnesium sulphide; the latter at once reacts upon the water present, magnesium hydrate and sulphuretted hydrogen being formed.

The cinders and other impurities of the tank-waste must be removed from the residue remaining after the just-described treatment. They cannot be left in the recovered lime, because, accumulating, they would make it unfit for black-ash mixing. These impurities are completely removed in a very simple manner, either by levigation or by passing the residue through a fine sieve. The cinders, coal, excess limestone, &c. contained in the tank-waste are heavier and coarser than the magnesia separated in the first operation; they amount to 25 or 30 per cent. of the whole dry weight of the tank-waste. The residue, thus purified, is now treated with more or less impure carbonic acid in order to recover the magnesium chloride and calcium carbonate, as previously mentioned. The way in which this is done will be apparent from the subsequent description of the apparatus.

The sulphuretted hydrogen from the first operation is now brought into contact with sulphurous acid and a solution of calcium or magnesium chloride, which can be done either in tubs or towers. In the latter case the H_2S should be introduced at the bottom of the tower, the SO_2 a little higher up. The precipitated sulphur settles down with striking rapidity, owing to the action of the chlorides; it is separated from the liquid by decantation or filtration, and the same solution used over and over again for running down in the tower. The gas-pipes must be easily accessible from without, for rapid cleaning. The requisite SO_2 is made by burning pyrites, sulphur, or sulphuretted hydrogen, or taken from any metallurgical process; it is either conveyed directly into the decomposer, or first condensed in an ordinary acid-condenser to a solution of SO_2 in water, or in a solution of $CaCl_2$ or $MgCl_2$.

This process is applicable not merely to tank-waste, but also to calcium or barium sulphate after their previous reduction to CaS or BaS; it also permits the utilization of the SO_2 evolved in many metallurgical operations. Its advantages are:—it is easy and safe in its execution; the working-up of the tank-waste costs much less time and wages than hitherto; at least 90 to 95 per cent. of the sulphur contained in the waste are recovered, as against 50 to 60 per cent.; 80 per cent. of the total lime are recovered as calcium carbonate adapted for black-ash mixing. The $CaCl_2$ and $MgCl_2$ are all recovered except the unavoidable mechanical losses, which can be made very small; in any case they are as nothing compared with the saving in wages and in the muriatic acid required in the processes hitherto employed. If the requisite SO_2 is made from pyrites, the production of sulphur can be increased by 50 per cent. over and above that recoverable from the waste. The ultimate residue only amounts to about 20 per cent. of the fresh waste, thus saving a great deal in carriage and depositing-ground.

Figs. 263 to 266 show the plant for working up the tank-waste by Schaffner and Helbig's patent, for a factory turning out 10 tons of soda ash per 24 hours.

1. *Vessels &c.*—A is the waste-hopper with carrying-screw; B, the mixing-vessel, with agitator; C, the decomposer for H_2S and SO_2; D, the sulphur-settler, with agitator; E, engine for driving the agitator; F, sulphur-filter; G, catch-well for the filtrate from F; H. pump for raising this liquid to the collecting-tank I, above the decomposers; K, sulphur-melting apparatus, with agitator;

L, engine for driving the agitator; M, cinder-settler, with agitator; N, engine for driving the agitators in B and M and the Archimedean screw in A; O, collecting-tanks for MgO and $CaCl_2$, with agitators (not shown in the drawing); P, pump for raising the MgO and and $CaCl_2$ liquor to Q, the carbonators; R, lime-mud settlers; S, lime-mud filters; T, wells for the $MgCl_2$ liquor filtering from R and S; U, wells for weak $MgCl_2$ washings; V, pump for conveying the strong $MgCl_2$ liquor back into the store-tanks W.

2. *Connexions &c.*—*a*, tramway for conveying the tank-waste; a_1, charging-screws at the waste-hoppers; *b*, pipe for taking away the H_2S; b_1 and b_2 pipes for admitting H_2S into the decomposers; *c*, pipe conveying SO_2; c_1 and c_2, pipes for admitting SO_2 into the decomposers; *d*, pipe connecting the decomposers with the chimney-flue; d_1 and d_2, branch junctions for the decomposers; *e*, open shoot for running the liquid into the sulphur-settlers; e_1, connecting-shoots between the sulphur-settlers; e_2, shaft for driving the agitators in the sulphur-settlers; *f*, pipe for carrying the sulphur-mud to the filters; f_1, overflow-pipes from the sulphur-settlers; f_2, pipe for running off the filtered liquid; f_3, pipe for running off the washings from the sulphur-filters; g_1, open shoot for the liquor running from the settlers; g_2, open shoot for washings from the same; h_1, suction-pipe for the sulphur-liquor pump: h_2, delivery-pipe, leading to the collecting-tank upon the decomposers; i_1 and i_2, distributing-pipes to the decomposers; *k*, tramway for conveying the filtered sulphur to the melting-apparatus; k_1 shoot for running water &c. from the sulphur-melters; l_1 and l_2, pulleys and gearing for the sulphur-melters; m_1, pipes for running the liquor from the mixing-vessels B; m_2, run-off for liquor from the lime-regeneration; m_3, run-off for cinders; m_4, tramway for the cinders; n_a, shaft for driving the charging-screws; n_b, shaft for driving the agitators in the mixing-vessels; n_m, shaft for driving the agitators in the cinder-settlers; *o*, distributing-shoot for liquor; p_1, suction-pipe of the pump for this liquor; p_2, delivery-pipe to the carbonators; *q*, pipe for CO_2 from the blowing-engines; q_1 q_2, branch pipes for passing CO_2 into the carbonators; r_0, pipes for taking the lime-mud from the carbonators to the settlers; r_1 cocks for clear $MgCl_2$ liquor; r_2, open spout for $MgCl_2$ liquor; s_1, cocks for running the lime-mud onto the filters; s_2, tramway for carrying the

filtered lime-mud to the drying-rooms; t_1, cocks for strong $MgCl_2$ liquor from the filters; t_2, cocks for weak $MgCl_2$ liquor and washing-water; u, open spout for liquors; v_1, suction-pipes of pumps for $MgCl_2$ liquor to be used over again in the process; v_2, delivery-pipe for the same; w, pipe for admitting $MgCl_2$ liquor into the mixing-vessels.

Details of Process.

(*a*) *Decomposition of Tank-waste by Magnesium Chloride.*—This is most easily understood from fig. 265. The waste is put in a damp state into the hopper A, and, by means of a carrying-screw, continuously conveyed into the decomposer B, where a certain quantity of $MgCl_2$ is present, and the waste is introduced until all the $MgCl_2$ is decomposed. B is closed air-tight; and an agitator works in it, kept air-tight by a gland. A steam-coil inside produces the necessary heat. The H_2S escapes through b. The $MgCl_2$ liquor is contained in W, and is run into B, by opening the valve u, as required. At the end of the decomposition the mass is discharged through m_1 into the open vessel M, provided with an agitator. The heavier portions, cinders &c., settle down and are discharged by a cock, m_3, into a bogie standing below. The liquor, consisting of a solution of $CaCl_2$ and suspended MgO, runs along through m_2 and the shoot o into the tank O.

(*b*) *Recovery of Calcium Carbonate.*—Best understood from fig. 265. The above liquor of $CaCl_2$ and MgO is pumped from the tank O, by the pump P, through the pipe p_2 into the carbonator Q. Through the pipe q CO_2 is forced through the liquor by means of a blowing-engine; it enters at the bottom of the carbonator by a number of small holes in the delivery-pipe, like the air in Weldon's oxidizers (see the Chapter on these in the next Book); or, more cheaply, a tower is employed, in which CO_2 ascending meets the mixture trickling down. At the end of the process the mass, now consisting of $CaCO_3$ and $MgCl_2$, is run into R. The clear $MgCl_2$ liquor runs through the cock r_1 and spout r_2 into the collecting-tank T (figs. 264 & 265). The $CaCO_3$ is discharged through s_1 into the filter S, and, after washing, put into the bogies s_2 in order to be conveyed to the drying-apparatus; the washings from it, still containing $MgCl_2$, run into U (fig. 264), and are used over again. A pump, V, conveys the $MgCl_2$ liquor through the pipes v_2 (fig. 265) back into the tank W. The recovered calcium car-

bonate works very well in the black-ash mixture; but it should be moistened with a little sodium-sulphate liquor before drying, to prevent its being blown away too easily. In this process the loss of $MgCl_2$ (5 or 6 per cent.), unavoidable in working on the large scale, can be made up by mixing some calcined dolomite along with the mass, its MgO being likewise converted into $MgCl_2$.

(c) *Recovery of the Sulphur.*—The decomposer C, for H_2S and SO_2, consists of a wooden tower filled with wooden prisms laid crossways; through b_2 the H_2S, through c_2 the SO_2 enters. I is a tank for $CaCl_2$ liquor, to run down in the tower. The precipitated sulphur, along with the $CaCl_2$ liquor, runs away through e to the agitating-tub D. The clear liquor runs away through f_1, and is carried by shoots (fig. 264) to the vessel G, from which it is again drawn by the pump H and forced through the pipes h_2 into the tank I on the top of the decomposing-tower. The sulphur-mud is discharged by f_0 into the filter F, and washed. The washings containing $CaCl_2$ pass through shoots also into the vessel G (fig. 264); the pure washings run to waste. Any gases escaping from the tower pass through the pipe d (fig. 263) into the chimney.

From the filter F the sulphur-mud is charged into bogies, and arrives at the apparatus K, where it is melted under steam-pressure (p. 665). Of each piece of apparatus (the tank-waste-decomposer B, the carbonator Q, and the decomposing-tower C) there is a pair; this is necessary for the uniformity of the work.

(d) *Production of Sulphurous Acid.*—This Schaffner and Helbig have found to be effected most conveniently by burning a portion of the H_2S, which is done without any difficulty. The pipe conveying the H_2S to the tower is provided with a branch which carries a portion of the gas into a burner. In this the gas issues from an iron pipe with small holes; a small coal-gas flame inflames the H_2S, and rekindles it if, from any cause, it should be extinguished. By means of valves the supply is so regulated that the proper proportion of H_2S and SO_2 is always present. The inventors have found that in this way H_2S can be burnt as easily as coal-gas—no doubt owing to the purity of the gas; the difficulties formerly experienced in burning H_2S were really owing to its dilution with indifferent gases.

While this is going to press, an application for a German patent (not yet granted) has been made by Dr. Aarland, for an improvement of Schaffner and Helbig's process. He dispenses with the

employment of magnesium chloride and treatment with carbonic acid, by employing for the decomposition of tank-waste a solution of calcium chloride at a high temperature and under pressure. The reaction is :—

$$CaS + CaCl_2 + H_2O = H_2S + CaO + CaCl_2.$$

The lime is obtained by levigating the residue; the $CaCl_2$ can be used over again. Of course it is not yet known how far this process will answer.

Treatment of the Drainage from old Tank-waste Heaps.

On p. 637 we have seen how this drainage can be made inoffensive; but the process there described was still not without expense. Mactear's process, on the contrary (patented Sept. 8, 1871, and fully described in a paper read before the British Association at Plymouth in 1877—reprinted in the Inspector's Report for 1877–78, p. 24), aims at a profitable treatment of such drainage. It was suggested by the annoyance caused by the enormous waste-heap near the St.-Rollox works at Glasgow, accumulated during more than forty years and covering about 10 acres. The rainfall alone would produce from it at least 13,000 gallons of drainage per day, which was at first discharged into the river Kelvin and then into the Clyde, doing the most serious mischief all along its course. This drainage-liquor cannot exactly be dealt with by the Mond or Schaffner process, since for either of these the sulphides and hyposulphites must be in such proportion that, on the addition of hydrochloric acid, there shall be no evolution of H_2S, but only precipitation of sulphur; but the drainage-liquors, containing far too much sulphide, give off a large amount of H_2S when treated with hydrochloric acid. Now Mactear's process simply consists in correcting the liquor by adding to it sulphurous acid, in one shape or another, so that the proper composition is attained, which Mond and Schaffner bring about by regulating the oxidation of the fresh tank-waste*. At first the drainage-liquors at St. Rollox were employed, instead of water, for lixiviating fresh tank-waste treated by the Mond process; but this was not found to answer, owing to the large evolution of H_2S. Neither was Mactear's first modification successful, viz. mixing the yellow

* Schaffner had, as far back as 1866, suggested the identical process afterwards brought out by Mr. Mactear.

liquor with a little lime and treating it with SO_2 before decomposing it by HCl; regulation was found too difficult.

The modification actually worked for some years past consists in using a solution of SO_2 in water. This is obtained either from pyrites or from the refuse sulphur from the process. The gas is passed through condensing-towers made of common flooring-boards well jointed and bound with iron corner-pieces and tie-rods, which have kept quite good after five years' use. The towers are filled with coke in three stages, cross joists dividing the tower into three parts. A tray with a large number of small lead tubes covered over with hydraulic lutes divides the water into fine streams. The sulphurous acid gas is led up one tower, down to the bottom of the same, and up another tower. The solution of SO_2 resulting is only of 2° Tw., which great dilution is certainly objectionable. It is run in a wooden shoot to the decomposing-vessel, and mixed on its way with sulphur-liquor of about 11° Tw.; in the decomposing-vessel they are met by a stream of hydrochloric acid; and the whole is kept carefully as near 63° C. as possible. With moderate care, but little H_2S is liberated; and the decomposition is regulated by a simple test. In order to learn the amount of HCl present, a burette is filled with yellow liquor; and this is run into a sample from the decomposing-vessel, to which a drop of a solution of iron has been added, till the mixture is blackened. The precipitated sulphur is treated as usual. The plant required consists of pumps and cisterns for yellow liquor, kilns for burning pyrites or sulphur, condensing-tower and water-supply, steam-boiler, wooden decomposers with stirring-gear, drainers for the sulphur, and steam melting-arrangements. The plant now at work at St. Rollox, and producing 30 to 35 tons weekly, cost £2019.

Mactear calculates the net cost of one ton of sulphur by his process at 61*s*., charging nothing for hydrochloric acid; but his calculation is an indirect one, and seems principally intended to prove that there is a larger profit made by his patent process than by employing the hydrochloric acid for making bleaching-powder. It does not, however, seem to have made much way beyond the St.-Rollox works, where alone 30 tons of sulphur are weekly produced by it.

A third modification (patented on Feb. 15, 1878, No. 885) is intended for use when very weak liquors (say from 5° to 8° Tw.) are to be treated. In this case a stronger solution of sulphurous

acid is made by the production of calcium bisulphite, or at least of a solution of calcium sulphite in sulphurous acid, which is used just as the weak SO_2 solution in the second modification. The calcium sulphite is extracted from old oxidized waste by grinding it in water to a milk and treating this with SO_2. More hydrochloric acid is, of course, required by this method; but less fuel is consumed, and the sulphur of the sulphite is gained.

A very ingenious process for treating the sulphurous drainage from old waste-heaps has been worked out (on the small scale) by Dr. R. A. Smith (Inspector's Report, 1877–78, pp. 9 & 29 *seq.*). It was suggested to him by the Dieuze process of treating tank-waste, and by the plan which the author had introduced at South Shields for dealing with the drainage from an old waste-heap, mentioned on p. 637, viz. mixing the yellow liquor with the settling mud of the Weldon manganese-recovery (that is, a mixture of calcium carbonate, gypsum, ferric oxide, manganese peroxide, &c.), which rendered the liquors quite colourless and inoffensive. The spent mixture, when thrown out and exposed to the air in shallow layers, became quickly oxidized, and could be employed over again for the same purpose. Dr. Smith took this matter up, and succeeded, after many experiments, in making it a continuous process. The solution to be freed from sulphur was put into a tall glass vessel; a little MnO_2 was added ($1\frac{1}{2}$ gramme to a litre), and air blown in. A siphon was employed for continually drawing off desulphurized liquor from the bottom of the vessel, its inner limb being protected by a calico-covered funnel against carrying away any precipitate; and a small stream of sulphur-liquor was run in continually at the top, so that the bulk of the liquid always remained the same. The sulphur-liquor entering the vessel was at once acted upon by the MnO_2, with formation of hyposulphite and free sulphur; the MnS formed was continually reoxidized by the air blown in. Complete desulphurization could only be attained if there was no more than $\frac{1}{10}$ per cent. of sulphur as sulphide in the liquor; this would necessitate larger vessels and more pumping, but is no great evil, as the liquor from the heaps could be run in in a proportionately small stream. The precipitate formed contains sulphur, calcium carbonate and hyposulphite, and manganese oxides; it must be removed from time to time and treated according to its nature.

Dr. Smith seems to think that this process may be employed on a large scale, not merely for waste-heap liquors, but also for making

barium hydrate. On p. 34 *seq.* he describes a number of experiments for extracting the sulphur from solid waste, the most interesting of which refer to Kraushaar's process (comp. p. 659).

As far as practical results are concerned, Dr. Smith extracted on the small scale as much as 72 per cent. of the sulphur in his precipitate; but some experiments made for him on a larger scale by Mr. Mactear had a less favourable result. For 100 parts of sulphur in the liquor there were obtained :—

In solution (as hyposulphite)	65·55
In precipitate	33·18
Lost	1·17

The precipitate contained still more sulphide and only 27·3 parts of sulphur in an available state. The amount of air employed was enormous compared with the work done; but Dr. Smith attributes the formation of so much hyposulphite first to this large excess of air, which consequently caused a loss of available sulphur. No doubt his idea will yet be further worked out.

CHAPTER XV.

HYPOSULPHITE OF SODA.

THE above is the name universally used in commerce and in manufacturing-practice for a salt the empirical formula of which is $Na_2S_2O_3$. Since the rational formula of the corresponding acid is now generally stated as $SO_2\langle{}^{OH}_{SH}$ (*i. e.* sulphuric acid in which one of the groups OH is replaced by SH), the modern nomenclature employed in some chemical treatises calls this acid *thiosulphuric acid*, and hence our salt *sodium thiosulphate*, reserving the name "hyposulphurous acid" for the acid H_2SO_2, discovered by Schützenberger and by him called "hydrosulphurous acid." But as any confusion with this latter acid is entirely out of the question here, we shall continue to employ the older name of sodium hyposulphite for the compound $Na_2S_2O_3$, as is still done by most of those concerned with it.

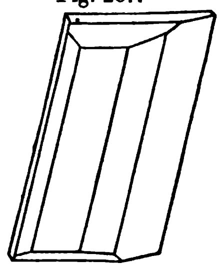
We subjoin the description of this salt to the Chapter treating of alkali-waste, because the latter is now practically the exclusive source for it, and the first attempts to utilize that waste, at least on the Continent, were connected with the hyposulphite (p. 650). It was discovered by Vauquelin in 1802, in alkali-waste (Wurtz, Dictionn. de Chimie, ii. p. 1535).

Crystallized sodium hyposulphite (Gmelin-Krant's Chemie, ii. p. 177) has the formula $Na_2S_2O_3+5H_2O$, and contains

Na_2O	62·1	25·02
S_2O_2	96·1	38·71
$5H_2O$	90	36·27
	248·2	100·00

It forms large, colourless, limpid columns of the monoclinic system (fig. 267). Spec. gravity 1·672 (Buignet) or 1·734 (Schiff); at 10° C., after melting and resolidifying, 1·736 (H. Kopp). It is devoid of smell, and has a cooling, afterwards bitter, somewhat alkaline and sulphurous taste. It has no alkaline reaction, and is stable in the air at the ordinary temperature, but effervesces at 33°. The crystals melt at 45° to 50° in their water of crystallization; the melted mass remains fluid for a long time after cooling. The water is almost entirely removed at the end of two months in a vacuum beside oil of vitriol; the remainder is expelled at 100° C. On heating, the salt becomes anhydrous at 215° C.; quickly heated, it is decomposed at 233° with separation of sulphur; the salt containing water suffers this decomposition even when slowly heated to 100° C. Heated beyond the above point the salt loses a little sulphur, and is ultimately transformed into a mixture of sodium pentasulphide and sulphate, almost black when hot, and reddish brown when cold.

Fig. 267.



On mixing 110 parts of the salt with 100 water the temperature sinks 18°·7 C. 100 parts of water dissolve, according to Mulder, at

16°,	20°,	25°,	30°,	35°,	40°,	45°,	47°,
65	69	75	82	89	98	109	114

parts anhydrous $Na_2S_2O_3$; according to Kremers, at

0°,	20°,	40°,	60°,
47·6	69·5	104·2	192·3

parts anhydrous $Na_2S_2O_3$; according to Schiff, at 19°·5, 171 parts of crystallized or 108·9 of dry salt, forming a liquid of specific gravity 1·3875.

By supersaturation (to which this salt is preeminently prone) a solution of 217·4 parts of $Na_2S_2O_3$ in 100 water at 0° can be obtained, which, under favourable conditions, remains liquid down to −10° C. The aqueous solution contains, according to Schiff:—

Spec. grav. at 19°.	$Na_2S_2O_3$ $+5H_2O$.	$Na_2S_2O_3$.	Spec. grav. at 19°.	$Na_2S_2O_3$ $+5H_2O$.	$Na_2S_2O_3$.
1·0052	1	0·637	1·1676	30	19·113
1·0211	5	3·185	1·1986	35	22·298
1·0529	10	6·371	1·2297	40	25·484
1·0807	15	9·556	1·2624	45	28·669
1·1087	20	12·742	1·2954	50	31·855
1·1381	25	15·927			

Opinions differ as to the stability of the aqueous solution, which is of special importance in volumetric analysis. According to Capaun, in closed vessels the solution deposits sulphur till only sulphite remains; with excess of air sulphate is formed. Others assert that the aqueous solution keeps without decomposition at the ordinary temperature, but is slowly decomposed on boiling.

Examination of Commercial Hyposulphite of Soda.—For photographic purposes it should be chemically pure, and especially absolutely free from sulphide, which is detected by the well-known reactions with lead acetate or sodium nitroprusside. Sulphuric acid is detected by barium chloride in dilute solutions (in concentrated solutions BaS_2O_3 would be precipitated); lime by ammonium oxalate. Sulphurous acid is detected by removing any sulphide by means of a zinc solution, filtering from any ZnS formed, acidulating with acetic acid, and adding sodium nitroprusside, which yields a red colour with SO_2. Coarser adulterations are most easily estimated quantitatively by treating the salt with decinormal iodine solution and starch up to blue.

In spirit of wine the salt is insoluble; hence its aqueous solution is precipitated by alcohol. Dilute hydrochloric or sulphuric acid does not change it instantly; but soon the liberated hyposulphurous acid is decomposed into sulphur (appearing as a milky precipitate) and SO_2. The decomposition of the salt with free iodine is noticeable, sodium tetrathionate and iodide being formed:

$$2Na_2S_2O_3 + 2I = Na_2S_4O_6 + 2NaI.$$

Of this reaction extensive use is made in volumetric analysis; and in gravimetric analysis the salt is employed, as at a boiling-heat it behaves in many respects like sulphuretted hydrogen towards metallic salts. Of great importance for photography is the circumstance that a solution of sodium hyposulphite readily dissolves silver chloride, and but little less readily silver bromide and iodide.

Sodium hyposulphite is employed to a considerable extent in papermaking and bleaching as "antichlorine," *i. e.* for neutralizing the effects of the chloride of lime, or free chlorine, left in the fibre from the bleaching process. According to Fordos and Gélis (Rép. Chim. Appl. 1859, vol. i. p. 384) 1 kilog. of hyposulphite would neutralize 1144 grams of chlorine, all its sulphur being oxidized to sulphate—

$$Na_2S_2O_3+8Cl+5H_2O=Na_2SO_4+SO_4H_2+8HCl;$$

but the author has shown (Berichte der deutsch. chem. Ges. xii. p. 404) that this is not the case; the action of hyposulphite upon chlorine is any thing but as simple as indicated by the above equation. Since a liberation of sulphuretted hydrogen is always perceptible, the following subsidiary reactions may take place:—

$$2Na_2S_2O_3=Na_2S_3O_6+Na_2S;$$
$$2H_2S_4O_6+4HClO+4H_2O=5SO_4H_2+4HCl+H_2S+2S.$$

The latter reaction has been proved to occur by Winkler (Dingl. Journ. cxcviii. p. 151).

Gélis (Moniteur Scientifique, 1879, p. 1023) maintains, against the author, the completeness of the reaction as formulated by himself and Fordos, provided that the exact conditions are adhered to which they have laid down for the analysis of hypochlorites. In any case these conditions could not be observed in the *industrial* application of hyposulphite; but even under these conditions the author has failed to get any thing like constant results. In very dilute solutions more chlorine is destroyed by hyposulphite than in more concentrated ones; in the latter case sometimes only one tenth of the action is exercised which the equation of Fordos and Gélis demands. The author replied *ib.* p. 1219.

For *preparing* this salt a large number of processes have been indicated, which must be mentioned very briefly, since practically

all hyposulphite is nowadays made from tank-waste, and with this the other processes would not compete, even if the consumption of the salt increased to many times its present amount: hence they have only a scientific or historical interest.

A. *From Sodium Sulphide and Sulphurous Acids* ($2Na_2S + 3SO_2 = 2Na_2S_2O_3 + S$).

1. Liebig (afterwards Capaun) saturates caustic soda liquor with sulphur by boiling, and passes SO_2 into the solution of Na_2S_5 till the liquor has become colourless, and no Na_2S, but only SO_2, can be found in it. (The former must be absolutely absent for photographic purposes.) The sulphur is filtered off, the solution boiled down, and crystallized.

2. Anthon ignites 4 parts sodium sulphate with 1 to 1½ part of coal, but not up to melting, and exposes the moistened mass to a current of SO_2 as long as any H_2S escapes; he then lixiviates with water and allows the solution to crystallize (Pharm. Centralbl. 1846, p. 418).

3. Stromeyer lixiviates the Na_2S, obtained as in No. 2, with water, and passes SO_2 through the solution (Dingl. Journ. clix. p. 428).

4. E. Kopp boils tank-waste with 10 to 15 per cent. of sulphur and 10 to 15 parts of water, passes SO_2 into the mixture, which is constantly turned up by paddle-wheels, and decomposes the calcium hypsosulphite formed by sodium sulphate solution (Bull. Soc. Ind. Mulh. 1858, p. 143).

5. In Schaffner's two-boiler apparatus for decomposing sulphur-liquors from tank-waste the SO_2 converts the calcium and sodium polysulphide and sulphhydrate into hyposulphite, which can be worked either for sulphur, as described previously, or for sodium hyposulphite by adding sodium sulphate.

6. Moody, on Feb. 2nd, 1877, patented exactly the same process as Nos. 1 to 3: he runs the solution of sodium sulphide down a tower in which SO_2 ascends.

B. *By combining Sulphur with Sodium (or Calcium) Sulphite.*

1. Liebig passes SO_2 into a solution of sodium carbonate till it is saturated, neutralizes with sodium carbonate, adds a solution

of caustic soda saturated with sulphur, filters, and evaporates to crystallization.

2. Lenz (Ann. Pharm. xl. p. 97) describes the same process without any essential variation.

3. Walchner (Ann. Pharm. xlvi. p. 235) heats a mixture of 32 dry Na_2CO_3 with 10 S, stirring it till the mass has ignited, by which process sodium sulphite is formed, and boils with sulphur.

4. The process employed in Lancashire in 1862, and described by Fleck (Wagner's Jahresb. 1862, p. 205), comes to the same thing; but the product of ignition is treated with a boiling solution of sulphur in caustic soda.

5. Schaffner (communications to the author) sometimes works up tank-waste desulphurized by his process (containing much calcium sulphite) by boiling with sulphur, lixiviating the calcium hyposulphite formed, and decomposing it with sodium sulphate.

Probably W. S. Losh first made sodium hyposulphite direct from *tank-waste* (*i. e.* without treatment with S or SO_2). His patent of July 6, 1852, prescribes allowing the waste to lie in the air for a week (in which case efflorescences of salts appear), then lixiviating in iron vessels, settling, drawing off the clear liquor into another vessel, and adding a solution of sodium hydrate (?) or carbonate till the sodium salt is formed. This is obtained by evaporating the solution and crystallization. The process of Losh was carried out by the Walker alkali-works until their stoppage in 1875, and supplied the greater portion of the sodium hyposulphite consumed in England.

Townsend and Walker (patent, Dec. 11, 1860) went a step beyond Losh, by running the solution from oxidized waste through a coke-tower in which an ascending stream of air, along with a little steam, assisted the oxidation of the polysulphides to hyposulphites. [This process, perfectly right in principle, could be carried out much more simply without a coke-tower by blowing in air by means of a Kœrting's blower &c. Only it should be tried whether there is not a considerable quantity of $CaSO_3$ and $CaSO_4$ formed in this way. Usually this is assumed not to be the case.]

The completely oxidized solution has an acid reaction; it is neutralized by milk of lime, evaporated to spec. grav. 1·25, and settled; it then chiefly contains calcium (and sodium) sulphite and hyposulphite. In the place of sodium carbonate, Townsend and

Walker employ the cheaper sodium sulphate for decomposing the calcium hyposulphite. The sulphate is dissolved to spec. grav. 1·18, and added until no more precipitate is formed.

The precipitate is washed a little. It contains chiefly gypsum, mixed with 2 to 5 per cent. of alkaline and earthy sulphites and hyposulphites; dried at 100° C. it furnishes a valuable material for paper-making, the calcium sulphate serving as a make-weight, and the sulphite and hyposulphite as "antichlorine." The solution drawn off from the precipitate is concentrated to spec. grav. 1·40; on cooling, sodium hyposulphite, with a little sulphite, crystallizes out. If concentrated to spec. grav. 1·65, the whole solidifies on cooling to a concrete mass. If in the place of sodium sulphate the sulphates of aluminium, potassium, or ammonium are employed for decomposing the calcium hyposulphite, the hyposulphites of those metals are obtained. Also calcium hyposulphite or sulphite can be boiled down to dryness [in this case the CaS_2O_3 is decomposed!] and employed as antichlorine. From the residue left after lixiviating the oxidized tank-waste, which contains much calcium sulphite, by boiling with caustic soda or potash the sulphites of these bases are obtained.

That the yield of hyposulphite can be largely increased by a suitable treatment of the sulphur liquor, was already set forth in Tullion's patent (Feb. 9, 1861), and still more explicitly in Noble's patent (July 6, 1861). To this Chapter belongs also partly the above-mentioned process of Kopp, but more especially the decomposition in Schaffner's two-boiler apparatus. The latter, of course, is not adapted for a continuous manufacture of hyposulphites, for which there must be an independent source of SO_2. Schaffner, indeed, lays down as a separate process the treatment of the yellow sulphur liquors by pyrites-burner gas (just as Kopp does for his liquors), continued till all the polysulphide and sulphhydrate have been transformed into hyposulphite, then adds sodium sulphate, and as to the rest proceeds like Townsend and Walker (Dingl. Journ. cxciii. p. 42). His other process (boiling desulphurized tank-waste with sulphur) has been mentioned on p. 705. After neutralizing the liquor treated with SO_2 by a little caustic or fresh sulphur-liquor, the requisite quantity of sodium sulphate is found by adding to a measured volume of the liquor an excess of standard Na_2CO_3 hot, filtering from the $CaCO_3$ and retitrating the excess of

Na_2CO_3 (the quantity of the latter used up being calculated into Na_2SO_4). The liquor drawn off from the calcium sulphate is evaporated to 86° Twadd., and allowed to crystallize. The product is pure enough for paper-makers and bleach-works, but for photographic uses is recrystallized in earthenware dishes. The Aussig works yearly make 200 tons of this salt.

It has also been proposed to make hyposulphite from the spent lime of gas-works just as from tank-waste, and from their spent oxide of iron by boiling with sodium sulphite.

Several proposals have been made for employing the cheaper *calcium* hyposulphite instead of the sodium salt. Unfortunately this can only be done in the rare cases where the salt is employed at the alkali-works themselves; for the calcium salt is not easily brought into a proper shape for transit, its solution being decomposed into calcium sulphite and sulphide, and the more quickly the more concentrated it is (E. Kopp). Only by evaporating at a very gentle heat can this be avoided and crystals of the formula $CaS_2O_3 + 6H_2O$ obtained. Such an evaporation is more expensive than decomposing by sodium sulphate. A patent of J. C. Stevenson's (March 18th, 1865) proposes avoiding that decomposition by evaporating in an iron vacuum-pan similar to those of sugar-works. The operation is to be carried on at a pressure of $\frac{1}{2}$ or 1 inch only, at a temperature of 43° C., till the spec. grav. of the solution attains 1·48; the crystals obtained on cooling are to be dissolved at 43° to a liquor of spec. grav. 1·45, and recrystallized from this.

Probably calcium hyposulphite boiled down by this process would still be dearer than sodium hyposulphite, if the interest on capital, repairs of plant, and the cost of keeping up the vacuum be counted. But even if it were cheaper, it could hardly be brought very extensively into the trade, since it decomposes, sometimes even in closed vessels, under unknown circumstances, to a yellow pasty mixture of sulphur and calcium sulphide; hence it would have to be used as fresh as possible.

Applications of the hyposulphites.—Chiefly, in photography, for fixing the positives; as antichlorine in paper-making and bleaching; for bleaching wool, straw, oils, ivory, bones, hair, &c. (as a source of SO_2); as anti-fermenting compound in sugar-making; as a convenient source for SO_2 in general; for making antimony-ver-

milion and ordinary vermilion in the wet way; sometimes as a mordant in dyeing and printing wool, silk, and cotton (as aluminium salt, according to Kopp); in the manufacture of several colours; in metallurgy (for extracting silver); for gilding- and silvering-liquors; as a chemical reagent, &c.

The *quantity* of sodium hyposulphite made in England in 1864 is estimated at 250 tons; in Aussig nearly as much is made.

END OF VOL. II.

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